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Principal Investigator,

Professor Haridwar Singh,

Visiting Professor,

D.I.A.T., Girinagar, Pune-411021, India

&

University of Pune, Ganeshkhind road,

Pune-411007, India.

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14. ABSTRACT

Ramjet propulsion provides efficient operation along with very high specific thrust and is very attractive for gun launch ramjet projectiles, hypersonic cruise vehicles and hypervelocity missiles. In the present investigation, Zr based fuel rich propellants in NC-NG matrix and HTPB matrix were evaluated for ballistic performance and mechanical properties. Although both the systems are attractive to produce higher density and high specific thrust, NC-NG based systems containing 30-60% Zr produce very high burn rates, comparable with modern advanced solid rocket propellants containing powerful oxidisers and metallic fuels. Zr based fuel rich propellants are very attractive for volume restricted systems and must be considered as potential candidates for air to air and air to surface missile applications. Based on the data generated in the present study on Zr based fuel rich propellants, and on the basis of similarity in properties of Zr, Ti and Ni, there is tremendous scope for research work on Ti and Ni based fuel rich propellants, as they are capable of producing higher specific thrust and their densities are very attractive (8.9 g/cc for Ni). Further, Ni produces stable combustion even at very low pressures of 10 Kg/Cm2

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Abstract

Hypersonic air breathing propulsion system has been in the minds of human being for a very long time. Ramjet propulsion provides efficient operation along with very high specific thrust and is very attractive for gun launch ramjet projectiles, hypersonic cruise vehicles and hypervelocity missiles. In the present investigation, Zr based fuel rich propellants in NC-NG matrix and HTPB matrix were evaluated for ballistic performance and mechanical properties. Although both the systems are attractive to produce higher density and high specific thrust, NC-NG based systems containing 30-60% Zr produce very high burn rates, comparable with modern advanced solid rocket propellants containing powerful oxidisers and metallic fuels. They are also attractive from the point of view of structural integrity of the propellant. It is possible to obtain very high burn rates (15-20 mm/s) by using 30-60% Zr. However, it is not possible to load more than 75% Zr in HTPB matrix and more than 65% Zr in NC-NG matrix for practical propellant compositions, as propellant slurry becomes very thick and it is not possible to cast propellant in mould or rocket motor. Zr based propellants are very attractive for volume restricted propellant systems. Unlike boron, no ignition related problem is visualised even in highly Zr loaded propellant formulations. Higher propellant density (1.9- 2.95 g/cc) along with low pressure index values are other attractive features of Zr based fuel rich propellant formulations. Their thermal decomposition and combustion behaviour has been studied using various modern techniques in the present investigation. While FRPs containing Zr in HTPB matrix decompose at higher temp., FRPs based on Zr in NC-NG matrix decompose at lower temperatures of 160-170 C. A probable mechanism on the combustion behaviour of Zr based fuel rich propellant has been suggested based on data generated and also considering earlier findings on Zr oxidation and combustion. It is believed that data generated in the present study will be very useful to develop practical powerful fuel rich propellants for ramjet and scramjet applications. It is also felt that further study on Nickel based fuel rich propellants, which appear to be very promising candidates, must be undertaken, in view of their unique characteristics of producing stable combustion at low pressures and very high density of Ni (8.9 g/cc).

1. Objectives:

Rocket ramjets are capable of realizing very high performance in ramjet mode. Major benefits of ram rockets include reduced missile weight, as oxidiser is not required to be carried along with the propellant. Solid fuel ramjets offer 200-400% increase in range over solid rocket motor of comparable size and weight. New generation of ramjets can deliver range, speed, continuous power supply and compactness for advanced propulsion systems. Metal powders like Al, Mg and B have been evaluated in the past for ramjet applications. Although, B is very attractive fuel due its higher heat of combustion, its high melting and

Boiling point cause serious ignition and combustion related problems. Moreover, it is aggressive in nature and causes propellant processing related problems. On the other hand,

Zirconium (Zr) has higher density (6.49 g/cc) and is capable of producing very high volumetric specific impulse. Its oxidation is a highly exothermic reaction and it is easy to ignite Zr even at high solid loadings in propellant compositions. Hence, zirconium is considered as a potential candidate for fuel rich propellants for ramjet applications. So far only limited studies have been conducted on zirconium based FRPs (fuel rich propellants). Keeping in view these facts, a research programme has been launched to study Zr based fuel rich propellants both in HTPB (Hydroxy terminated poly butadiene) and NC-NG (nitro cellulose- nitro glycerine) matrix. In the present investigation, systematic data on ballistic properties of FRPs containing high percentage of Zr has been generated. In addition, attempts have been made to understand mechanism of decomposition and combustion of FRPs based on the information generated on partial heat of combustion, thermal decomposition, using DTA technique, hot stage microscopy and Scanning electron microscopy (SEM) studies.

2. Introduction:

Hypersonic air breathing propulsion has been on the minds of human kind for a very long time. Solid propellant ram rocket (SPR), known as ducted rocket or air breathing propulsion systems belong to ramjet family. In 1913, Renelorn of France was first to recognize the possibility of using ram pressure in a propulsion device. Albert Fono of Hungary was granted a German patent in 1928 on a propulsion device that contained all elements of a modern ramjet and was intended for supersonic flight. During 1950s and 60s, efforts were made in USA and Germany to investigate this powerful propulsion system. In Russia (then USSR), SPR development was carried out, leading to application of IRR (Integrated Rocket Ramjet) propulsion for SAM-6 anti-aircraft missile. This became operational during 1967. Amongst the other operational missiles, propelled by ramjet are American Bomarc (1957) and British Blood hound (1959), followed by others during 1970’s (1-3). There were not many R&D activities during the period 1970s and 80s, although ONERA, France demonstrated SPR propulsion system during 1976 and MBB Germany in 1981.The basic design of SPR is given in Fig. 1.

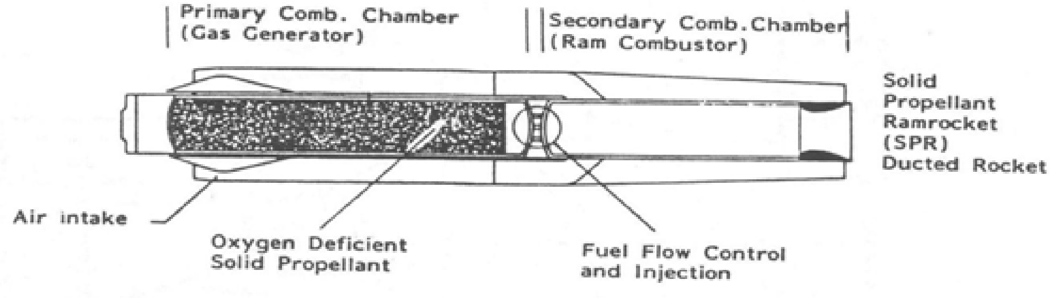


Fig. 1: Basic design of SPR

In SPR an oxygen deficient solid propellant called as a fuel rich propellant (FRP) burns in the primary combustion chamber as gas generator propellant. Fuel rich combustion products of primary chamber are passed through the secondary combustion chamber, known as ram combustor, where they mix and burn with ram air supplied by the air intake system.
Since atmospheric air is used in SPR for full combustion, the incorporation of solid oxidizer in propellant reduces the energy in terms of specific impulse (Isp). SPR permits inclusion of high proportion of energetic ingredients such as oxidizers and metallic fuels like Al, Mg, B, C, Zr etc. in the propellant composition. The high temperature of combustible products injected in the ram combustion allows high combustion efficiency and eliminates additional device to initiate the ignition during ram rocket combustion. Thus, the major advantages of ram rockets include reduced missile weight (as oxidizer is not carried along with propellant) as compared to conventional solid rockets. High density materials incorporated in FRPs produce high volumetric energy due to higher heat of reaction with oxygen and improvement in the propellant density. Currently, there is renewed interest in ramjet propulsion for futuristic supersonic flight missions like Cruise missiles for air to air applications and other defence missile systems. Ramjet appears to be the most efficient solution for these missions. European long range air to air missile, Meteor, propelled by a ducted rocket engine is one of such examples. Ramjet propulsion provides efficient operation along with very high specific thrust to overcome drag. In the field of gun launched ramjet projectiles, SFRJ (solid fuel rocket ramjet) is highly promising propulsion system. Supersonic muzzle velocity provides operating conditions for ramjet propulsion.

Possible applications for scramjet include hypersonic cruise vehicles, hypervelocity missiles and air breathing boosters for space applications. For hypersonic missiles, air breathing system operating below Mach 6, using hydrocarbon fuels are preferred, in view of volumetric and operational constraints. One of the very attractive missions identified for scramjet powered propulsion vehicle is the Mach 8 cruise missile as standoff fast reaction weapon or a long cruise missile. Typically, in IRR propulsion booster rocket provides a high thrust for short duration, followed by sustained thrust for long duration in sustainer phase. All modern ramjet missiles use IRR concept, where combustion of high energy solid propellants (composite or composite modified double base propellant) provides high thrust in boost phase. Subsequently, ramjet mode starts the nozzle and ramjet power begins. Basic ramjet engine consists of an inlet, diffuser, combustion chamber and exhaust nozzle (Fig-2)

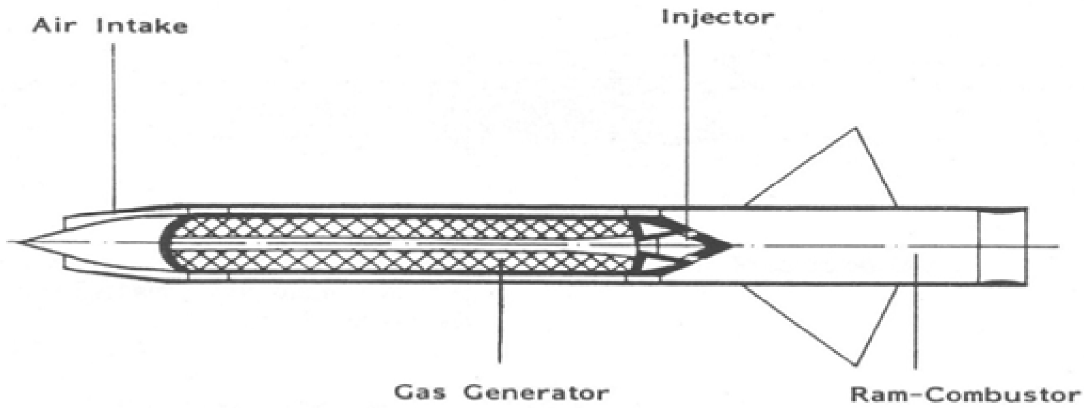


Fig-2 Basic ramjet engine

The unique combination of heat addition in supersonic air stream with variable shock system and absence of a geometric throat permits a scramjet to operate efficiently over a wide range of flight conditions. This means a nozzle subsonic combustion ramjet at low flight mach number (M=3-6) and a supersonic combustion ramjet at high mach number (M>5). The performance of an air breathing engine is always higher than that of a rocket and by using scramjet this advantage can be extended to a higher Mach region. Since, most of the literature on zirconium based solid fuel rocket ramjet is scattered, patented, classified and has not been reviewed, and keeping in view of their tremendous potential to offer very high specific thrust, an attempt has been made in this paper to cover R&D work done so far and discuss important features of metallised FRPs in general and Zr based FRPs in particular including their combustion behaviour.

During 1950s USA had planned to field a radar- beam riding anti air weapon capable of delivering around 4500 Kg warhead at higher ranges. The first project in this series was the cobra ramjet. The purpose of this exercise was to demonstrate that a ramjet can produce requisite thrust to cruise at supersonic speed. This was followed by the test of large diameter ramjet called burner test vehicle (BTV). Advanced low volume ramjet (ALVRJs) was approved in USA during 1967; its propulsion system consisted of a liquid fuel ramjet with an integral solid rocket booster. The booster propellant was case bounded of star perforated design.

Pein and Krishnan (4) have investigated influence of propellant composition, nature of fuel, oxidiser and binder on ducted rocket performance as well as influence of primary chamber fuel in secondary chamber. Binders were based on HTPB and GAP

Fry (5) has given an excellent account of ramjet propulsion technology evolution covering first to fourth generation scramjet development. During late1990s, NASA established long range goals for exploration of space. Third generation launch system of NASA is expected to be fully re-usable and should be operational by 2025. The main objective of this launch system is to reduce cost of launch by a factor of 100 and improve safety by a factor of 10,000 over current propulsion devices. Recently, many international joint R&D activities have commenced. A joint French-Russian research programme for wide range of ramjet has been initiated to develop technology for re-usable space launchers. Another French effort, leading to high speed dual mode ramjet propelled vehicle at mach 4-8 is expected during the period 2010-2012. Japanese national aerospace laboratory has commenced design, fabrication and testing of a side wall compression type scramjet engine (6-14).

It is apparent from above account that scramjet development has come of age during 1990-2000, with good understanding of the technology that will enable ramjet powered flights in future. Thus, scramjet technology developments are underway in many countries of the globe to capitalize on pay offs that hypersonic speeds and long range can provide. U.S. Navy has initiated a programme in 2002 to demonstrate ramjet propulsion technology to enable hypersonic long range missiles.

Most of R&D work on Zr and Ti based FRPs is of recent origin. Although, these fuels are well known and have very high potential due to their higher densities and high volumetric heating values as compared to other metallic fuels like Al, Mg, etc. Use of other metallic compounds like metal hydrides, metal borides and metal alloys has also been recommended to increase heat content of FRPs. Further, ultrafine Zr powder ignites very easily and burns extremely rapidly producing high heat.

We have published a review article on “Metalized FRPs for solid rocket propellants” during 1994. This paper covers the details of various formulations based on different metallic fuels. This article covers most of the R&D work carried out up to 1990 in the field of metalized fuel rich propellants based on Al, Mg, B etc without any specific reference on the type of metal powder used (15). Most of further R&D work carried out in this area are covered in the papers published during the period 2004-2007 as per references given under 17-30. Thomas has reported results of burning rates of Al, Mg and their alloy based formulations with HTPB as binder and AP as oxidizer. In general, burn rates were lower with increasing metal content. Lower pressure index values were obtained for aluminized formulations containing 45-50% Al. Inclusion of copper chromite as burn rate catalyst increased burn rates by almost 150%. At same oxidizer level, Mg based formulations produce higher burn rates. Invariably, Al-Mg alloy based formulations produce higher burn rates than individual Al or Mg based formulations. This could be due to the reason that Al-Mg alloy has lower ignition temperature and higher burn rates than pure Al and Mg based formulations. Greater reactivity of Al in the combustion process in presence of Mg would be an added advantage. Addition of Al sensitizes thermal decomposition of AP, whereas Mg-Al alloy induce lower ignition temperature by 100^0C. This indicates higher reactivity of AP with Mg-Al alloy (31).

Most of the propellant formulations studied earlier were based on HTPB-Al/Mg/Al-Mg alloy and boron. However, now the trend is to use energetic binders and energetic plasticizers in place of conventional inert binders and inert plasticizers like organic phthalates and acetates. FRP formulations based on poly BAMO and poly NIMMO are capable of giving Isp of the order of 900-1200 sec. Of late, GAP (Glycidyl azide polymer) based fuels are being evaluated for IRR applications. Low molecular weight GAP (500-700) can be used as energetic plasticizer, whereas high molecular weight GAP (2500-4000) can be used as energetic binder cum fuel. GAP has another unique advantage of producing self sustaining burning in primary rocket motor without any oxidizer. An important attribute of azide based polymers like GAP and BAMO and their co-polymers is their positive heat of formation, resulting in highly exothermic reactions during decomposition. This can be considered as an added advantage, as butadiene based polymers like HTPB and CTPB (carboxy terminated poly butadiene) decompose in an endothermic mode, thereby giving heat sink effect to propellant combustion. A few formulations based on Zr-AP- GAP have also been studied recently. Inclusion of GAP is reported to enhance burn rates significantly (32).

Lou etal (33) has patented a FRP composition containing 80-90% Zr of 2-4 micron along with 10-20% AP. They claimed high burn rates and low burn rate sensitivity by controlling particle size distribution of Zr. Harry (34) has patented high gas producing FRPs containing up to 40% Zr. Reed et.al. (35) have patented an improved Zr based ramjet fuel using hydroxyl terminated fluorocarbon as binder. Thus, only limited numbers of studies have been conducted on Zr based fuel rich propellants for ramjet and scramjet applications.

While studying effect of fuel properties on specific thrust of a ramjet engine, Gany et al (28) have analyzed different elements for their maximum potential for maximum specific thrust for volume restricted system and found that for maximum thrust Mg, Al and Zr are most promising. These metals produce three times higher combustion energy per unit mass of air than hydrocarbon fuel. This means possibility of achieving 50% higher maximum specific thrust with a penalty of reducing Isp.

We have reported recently that 20-40% Zr with HTPB as binder and with AP as oxidizer produces stable combustion in 1-9 MPa pressure range. With 20% Zr, burn rates varied between 3.7 mm/sec and 6.7 mm/sec in the same pressure range, whereas 40% Zr produced burn rates varying between 2.3 mm/s and 5.2 mm/s. The pressure index values of these formulations were around 0.34 and density obtained was 2.03 g/cc for 40% Zr based formulations. NC-NG matrix with 30% Zr produced high burn rates of 6-19 m/sec in the pressure range of 1-9 MPa. Whereas in case of 40% Zr based formulations, burn rates varied between 12 mm/sec and 17 mm/sec in pressure region of 3.1-9 MPa. Cal-val (Partial heat of combustion) of these formulations was in the range of 1000-1200 cal/gm.Mechanical properties of NC-NG based FRPs were very high (4-7.7MPa) and percent elongation was around 30% (36).

Kubota et al (37- 38) have studied the combustion of Zr & Ti particles with KNO_3 and found that while Ti particles react exothermally at 970K with decomposed gases of KNO_3, Zr particles react at 700K with liquefied products of KNO_3. Burning rate of Ti-KNO_3 based formulations was found to be more sensitive to pressure than that of Zr-KNO_3 based formulations. They have suggested that major exothermic reaction in the combustion wave of Zr-KNO_3 takes place in the condensed phase and burn rates are dependent on oxidizer to fuel ratio. Burning rate of Zr-KNO_3 was found to be less dependent on pressure and heat generated by exothermic reaction between Zr particles and gasified KNO_3 was higher with increase in Zr fraction. The activation energy was found to be 105 kJ/mole for Zr-KNO_3 composition, whereas the same for Ti-KNO_3 based formulations was 200 kJ/mole. In addition, moderate ignition temperature of these compositions also helps in producing stable combustion. These results indicate that Zr based compositions decompose at lower temperature than Ti based formulations.

We have also reported comparative effect of metallised fuel rich propellants on ballistic properties and found the 20-40 % Zr based compositions can produce Isp of 570 sec at air to fuel ratio of 15. In terms of density-specific impulse, Zr based compositions are capable of producing very high performance (900-2006 Kg-s/cubic meter × 10^3), followed by Ti based compositions which can produce density-specific impulse of 800-1850 Kg-s/ cubic meter × 10^3 (32). The findings of this study clearly bring out very high potential of Zr based fuel rich propellant for futuristic applications. Moreover, Zr can be used alone as metallic fuel as well as in combination with other metal fuel to achieve superior combustion efficiency.

The above review indicate that Zr based formulations are very attractive and highly promising for both ramjet and scramjet applications, particularly where designer has the constraint of restricted volume. However, detailed and exhaustive studies on formulation, processing and evaluation including their thermal decomposition and combustion behaviour are needed to understand their combustion mechanism. Hence, this research program was launched.

3. Experimental:

In present study, zirconium powder based fuel rich propellant compositions were processed by slurry cast method, adopting two different binder systems viz. HTPB and NC-NG based binder systems (16). Starting materials like AP, HTPB, Zr powder etc of high purity were procured from trade, whereas NC & NG were obtained from ordinance factories. Broad specifications of the materials used in the present study are given below.

a) Zirconium powder – Purity- Min- 98%, active Zr content 92%, Iron 0.5% Max., particle size- 5-7 µ.

b) AP- Purity- Min- 99%, pH 5-6, particle size- coarse -250 -270 µ, fine- 8- 10 µ.

c) HTPB- Mol. Wt. 3200 – 3500, Hydroxyl number 40 – 50 (mg KOH /g), viscosity at 30^{o}C is 60 -70 poise, specific gravity- 0.92, functionality- 1.9 -2.1, trans- 64%, cis – 16%, Vinyl content- 20%.

d) Nitrocellulose (NC) – Spherodical nitrocellulose (SNC) made in pilot plant of HEMRL, Pune containing 90% NC of 12.2% nitrogen, 7.5% NG and 2.5% carbamite was used. SNC has pot life of 3-4 hrs. Particle size – 30-40 µ, bulk density 0.90 g/cc.

e) Nitroglycerine (NG) – Nitrogen content 18.2%. NG was extracted from dynamite containing 65% NG and 35% Kiesel guhr by water percolation method.

f) Low molecular weight GAP- (molecular weight 500-600) made in the laboratory from poly epichlorohydrin and sodium azide was used. GAP used has OH value of 336 mg of KOH/g. It has TG of -50^{o}C and specific gravity of 1.25 g/cc.

HTPB based fuel rich propellant compositions:

HTPB binder was prepared by using HTPB: DOA in the ratio of 65:35. It was heated at 50^{o}C for 30 min with continuous stirring under vacuum to remove moisture. Zr was then added in small instalments with continuous stirring, followed by slow addition of oxidiser Ammonium perchlorate (AP). Toluene di-isocynate (TDI) was added as a curative with –NCO: OH ratio of 1.1:1. Propellant slurry was evacuated under vacuum to remove any entrapped air. **It was found that it is difficult to process propellant formulation, when Zr content was more than 75% in HTPB matrix**, as slurry develops very high viscosity and becomes very thick and sticky and hence cannot be cast. In view of this, propellant could not be processed beyond 75%. Curing was carried out at 75^{o}C for 5-7 days in water jacketed oven.

NC-NG based FRP compositions:

Casting liquid (desensitized NG) was prepared by mixing nitroglycerin (NG), triacetin and 2-NDPA in 80:18:2 proportions. Mixture was de-aerated by applying vacuum till moisture content was reduced to 0.2%. SNC was added to casting liquid in a planetary mixture. Zr powder and AP were added in instalments to double based propellant matrix. Mixing was carried out for 45 min under vacuum at 25 C. Propellant was cast in an aluminium mould under vacuum and curing was carried out at 60^{o}C for 5-7 days. In case of GAP based compositions, conventional plasticisers DEP (Di-ethyl phthalate) was replaced by GAP. **It was found that no propellant formulation can be processed, if Zr content is more than 65% in NC-NG matrix.**

Zirconium based FRPs were subjected to following studies to generate experimental data;

- Cal-val (partial heat of combustion) was determined at ambient condition, using Parr Bomb Calorimeter of Joulius Peters Make. The correct Cal-Val was obtained by subtracting factor for air correction. The destandard deviation in Cal-Val was of the order of ±2 cal/g.

- Burn rates were determined at different pressures by Crawford/ acoustic bomb under inert atmosphere. Strands of 6 mm dia. × ~150 mm length were made and inhibited for burning rate studies.

- Thermal studies were carried out by using DTA technique. DTA studies were carried out under atmospheric conditions at a heating rate of 10 ^{o}C/min.

- Laser ignition studies were carried out by semiconductor diode (In/Ga/As) laser source (wave length of 980 nano meter in IR region) with input of 6V DC battery, output of 1W Quasi CW and pulse duration of 50 ms and 100 ms were used.

- Hot stage microscope of GMBH Weitzler make was used. The method involved placement of a thin cross section of propellant sample in the micro furnace which was heated at the rate of 10 oC/min. Physical changes were recorded at different temperatures and photographs were taken using Leica camera.

- Scanning electron microscopy (SEM) – In order to understand combustion mechanism of fuel rich propellants, propellant samples were subjected to SEM studies using equipments of JOEL make (JSM-200). Coated samples were subjected to 25 KW acceleration voltage and photographs were taken at X750.

- Mechanical properties – Universal material testing machine (installed model 1185) was used to determine mechanical properties particularly tensile strength (TS) and elongation (% E). ASTM-D638 standard were followed for sample preparation.

4. Results and discussion:

In the first phase of study, Zr based propellants containing 20-70% Zr in HTPB matrix were studied. Ammonium perchlorate (AP) content was varied from 10 to 60%, whereas HTPB content was kept the same (20%) in all the formulations. Compositional details and results of burn rates at different pressures are given in Table 1& 2.

Table 1- HTPB based FRP compositions

Ingredients used	Compositions					
	1	2	3	4	5	6
Zirconium	20	30	40	50	60	70
AP (coarse: fine – 70:30)	60	50	40	30	20	10
HTPB	20	20	20	20	20	20

Table 2- Results of burn rates at different pressures of HTPB based FRPs compositions

Compositions	Percent Zirconium	Burn rates(mm/s) at MPa						Pressure index (η)
		1	2	3.5	5	7	9	
I	20	3.7	4.2	5.2	6.2	6.4	6.7	0.27
II	30	3.1	3.8	4.7	5.3	5.9	6.6	0.34
III	40	2.3	3.2	3.6	4.5	4.9	5.2	0.37
IV	50	2.2	2.5	2.8	3.1	3.4	4.2	0.29
V	60	-	2.0	2.4	2.7	3.0	3.9	0.32
VI	70	3.9	4.3	5.1	5.6	6.1	6.9	0.26

It can be seen from the results obtained that burning rates decreased with increase in percentage of Zr. However, surprisingly burn rates were very high with a FRP containing 70% Zr and burn rates obtained were very close to those obtained with 20% Zr. This is, however, contrary to the expectation, as with increase in Zr content and decrease in AP content, formulations become heavily fuel rich and are therefore not expected to produce high burn rates. This aspect needs further detailed investigation. All the compositions studied produced stable and sustained combustion in the entire pressure range of 1-9 MPa. These results indicate that heavily Zr loaded propellant compositions are capable of producing stable combustion even at low pressures and are well suited for gas generators needed for integrated rocket ramjet (IRR). These compositions produced an average pressure index value of 0.32.

Results of Cal-Val, density and mechanical properties of HTPB based FRPs are given in Table-3

Table 3- Results of Cal-Val, density and mechanical properties of HTPB based FRPs compositions

Properties	Propellant Compositions					
	I	II	III	IV	V	VI
Cal- Val (cal/g)	863	1015	1163	1260	1346	-
Density (g/cc)	1.77	1.91	2.03	2.2	2.37	2.95
Mechanical T.S.(Kg /cm^2)	5	5	5	5	5	6
Percentage elongation	10	11	11	10	11	12

Results shown above indicate that both Cal-Val and density increased with increase in the concentration of Zr. Cal-Val increased from 863 cal/g to about 1350 cal/g, when Zr content was increased from 20 to 70%. Likewise, density increased from 1.77 g/cc to 2.95 g/cc. However, there is not much change in the tensile strength (TS) and percentage elongation (% E), which remained at the level of 5 Kg/cm^2 and 11% respectively. Burn rates and Cal-Val results are graphically presented in Figure 3, 4 and 5.

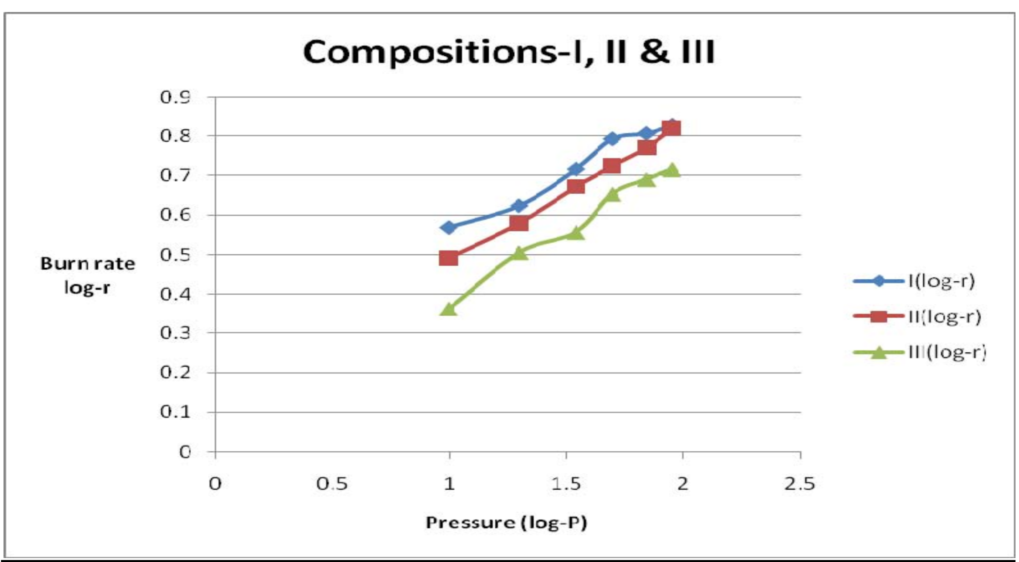


Fig 3. Results of burn rates of propellants containing HTPB and Zr.

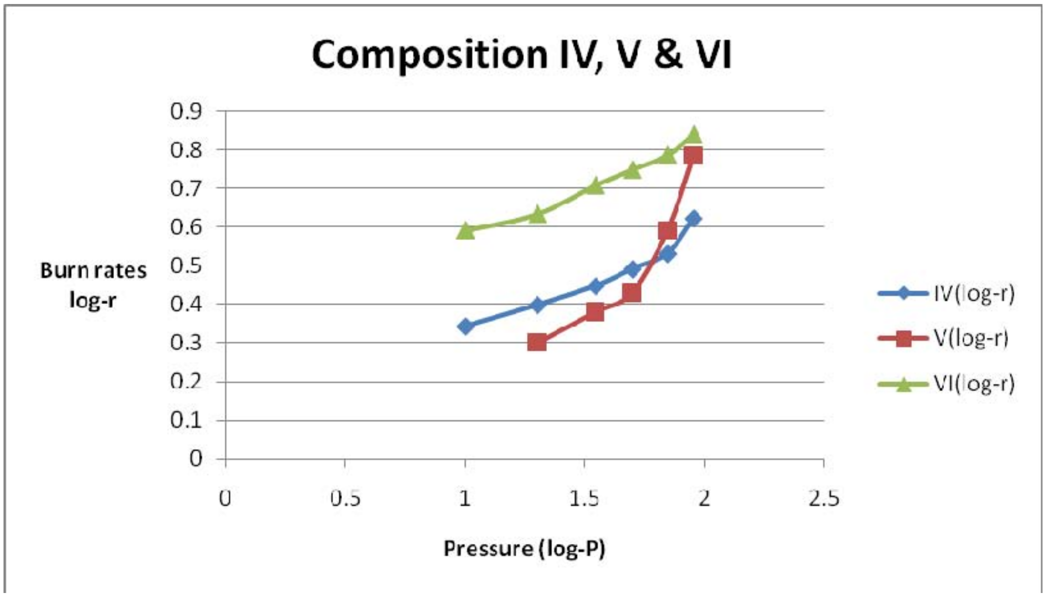


Fig 4. Results of burn rates of compositions containing HTPB and Zr.

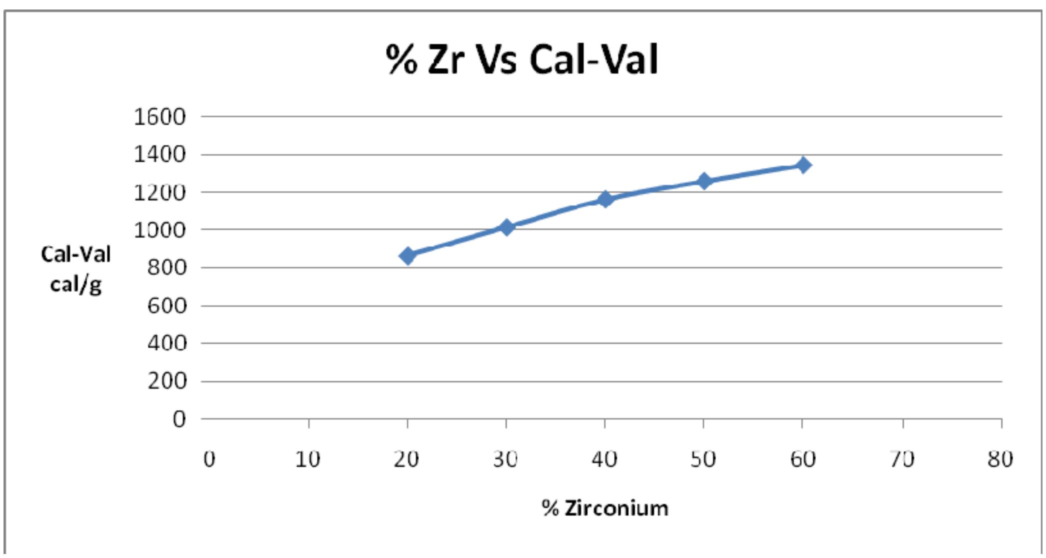


Fig 5. Results of Cal-Val of FRPs containing 20 to 70 % Zr.

In order to understand combustion behaviour of heavily loaded Zr powder more than 60%, another set of experiments were conducted using 65 to 75% Zr. Since, it was not possible to process propellants containing more than 75 % Zr, further experiments were discontinued. The compositional details and the results of burn rates are given in Table 4 and 5.

Table 4- HTPB based FRP compositions

Composition / Ingredients	1	2	3
Zr **(%)**	65	70	75
AP- 200 µ (60%) AP- 50 µ (40%)	12 8	9 6	6 4
HTPB binder (%)	15	15	15

Table 5- Results of burn rates at different pressures of HTPB based FRPs compositions

Composition	Burn rates at pressures (mm/s)				Pressure index (η)
	3	7	9	11	
I	-	5.3	6.3	7.2	0.61
II	3.5	4.5	-	6.5	
III	Did not ignite	Did not ignite	Did not ignite	Did not ignite	

These results indicate that burn rates reduced with increase in Zr content from 65 to 70 %. The variation in burn rates with 70% Zr in first and second set of experiments could be due to change in the composition, as concentration of oxidiser AP and its particle size distribution in two sets of experiments were different. It was found that a propellant composition containing 75% Zr did not ignite at any pressure studied. Use of even very powerful ignition system like cordite (NC-NG based) did not help in resolving ignition related problems.

In the second phase of study, Zr based formulations in NC-NG matrix were studied. In the first set of experiments, 20 to 40% Zr along with 30 percent each of NC and NG were used. AP content was varied from 0 to 20 % in these formulations. Compositional details and results of burn rates are given in Table 6 and 7.

Table 6- Compositional details of NC-NG based FRP compositions

Ingredients used	I	II	III
Zr	20	30	40
AP	20	10	-
NC	30	30	30
NG	30	30	30

Table 7- Results of burn rates of Zr based compositions in NC-NG matrix.

Compositions	Percent Zirconium	Burn rates(mm/s) at MPa						Pressure index (n)
		1	2	3	5	7	9	
I	20	6.2	8.6	10.7	14.2	16.9	18.9	0.51
II	30	5.6	7.4	9.8	13.6	15.1	17.9	0.53
III	40	Ext*	Ext*	7.8	12.2	15.0	17.4	0.85

It can be seen from the results obtained that 20% Zr in NC-NG matrix produced very high burn rates, ranging from 6 mm/s to 19 mm/s in the pressure range of 1- 9 MPa. 30% Zr also produced sustained burning rates in the entire pressure range studied and pressure index values were around 0.52. In case of 40 % Zr based formulation without any additional oxidiser, burn rates varied between 8 to 17.5 mm/s in the pressure range of 3- 9 MPa. However, propellant did not ignite at 1 and 2 MPa pressure, probably being highly fuel rich in the absence of oxidiser.

Results of density and mechanical properties of ZR based compositions are given in Table- 8.

Table 8- Results of mechanical properties of Zr based compositions in NC-NG matrix

Properties	Compositions		
	I	II	III
Density (g/cc)	1.92	2.07	2.25
Mechanical T.S.(Kg /cm^2)	19	40	77
Percentage elongation	33	28	18

Density increased from 1.9 0g/cc to 2.25 g/cc with increase in concentration of Zr. Surprisingly, tensile strength increased considerably from 19Kg/cm 2 to 77 Kg/cm2 with increase in Zr content with reduction in percentage elongation with increase in Zr content. These results are suggestive of the fact that Zr acts as powerful filler/ reinforcing agent in NC-NG matrix.

In continuation of this study, effect of 50 -60 % Zr in NC-NG matrix was studied without any additional oxidiser like AP, except in one case where along with 60% Zr, 5% coarse AP was also added to ensure sustained combustion. Additional oxidiser was deliberately eliminated in these formulations, as 20-40% Zr based formulations studied earlier produced high burn rates (Table-7). Compositional details and results of burn rates are given in Table- 9 and 10.

Table 9- Compositional details of NC-NG based FRP compositions

Composition:	I	II	III
Zr	50	55	60
NC	25	20	15
NG	25	25	20
AP (200 μ)	-	-	5

Table-10: Burn rates of fuel rich propellant Compositions (NC-NG matrix).

Composition	Burn rates at pressures (mm/s)				η
	3	4	5	7	
I	7.5	8.7	9.7	12.5	0.61
II	-	10.9	11.2	-	0.13
III	12.3	13.6	14.1	15.4	0.30

These results indicate that propellant compositions containing 50-60% Zr in NC-NG matrix produced not only sustained combustion, but also produced high burn rates. In case of 60% Zr based composition, burn rates varied between 12 and 15 mm/s in the pressure range of 3-7MPa. Invariably, pressure index values were lower for these formulations. Since it was not possible to load more than 60% Zr in NG-NG matrix, further experiments were discontinued.

5. Thermal decomposition and combustion studies of Zirconium based propellants:

Thermal analysis was conducted using DTA (Differential thermal analysis). Hot stage microscopy (HSM) and Scanning electron microscopy (SEM) studies were conducted to understand combustion behaviour of FRPs.

DTA was carried out using indigenously fabricated furnace. Programmer Stantom Redcraft was used for programmed heating. DTA studies were carried out at heating rate of 10^{o}C/min. Hot stage microscopic studies were undertaken, using hot stage polarising microscope. This experiment involves placement of thin cross section of propellant sample in micro furnace, which is heated at the rate of 10^{o}C/min. Physical changes of samples are recorded at different temperatures.

SEM study were carried out using GEOL make instrument (model- JSM-200). Propellant formulations with 30% Zr, 30% NC, 30% NG and 10% AP were selected for SEM studies. Likewise, another propellant composition in HTPB matrix containing 40% Zr, 40% AP and 20% HTPB was selected for SEM studies. Propellant samples were coated by thin layer of gold under evacuated condition and samples were then subjected to 25 KV acceleration voltage. Photographs were taken at the magnification level of X × 750.

5.1. Results of DTA studies

The inception (Ti) of decomposition of NC-NG-AP based propellant containing Zr commenced at 158^{o}C and was completed at 192^{o}C with peak temperature of 178^{o}C. Likewise, NC-NG-AP and Zr based compositions containing energetic plasticizer GAP in place of DEP (diethyl phthalate) decomposed between 156^{o}C and 190^{o}C with peak temperature of 175^{o}C. In case of AP- HTPB - Zr based composition; decomposition commenced at 243^{o}C and was complete at 338^{o}C, with peak temperature of 323^{o}C. These results indicate that decomposition behaviour of fuel rich propellants containing Zr is more or less same as that of conventional double base propellants, which are known to decompose se between 160^{o} C and 200^{o}C. Like conventional composite propellants containing AP-HTPB and metal powder, FRPs containing Zr decomposed in temperature region of 240 -330 ^{o}C. Difference of 2^{o}C to 3^{o}C in decomposition for GAP based FRP composition cannot be considered as a significant difference and in fact it will be too early to state that inclusion of GAP brings down decomposition temp.

5.2. Hot stage microscopy

Results of hot stage microscopy are given in Table-11 below-.

Sr. No	Experimental condition	Observations	
		40% Zr+ 40% AP + 20% HTPB	30% Zr +30% NC+ 30% NG + 10% AP
1	Propellant matrix at ambient temperature.	Pale bluish	Brown
2	Evolution of gases	150^{o}C - 160^{o}C	100^{o}C- 110^{o}C
3	Decomposition of matrix (contraction)	210^{o}C - 220^{o}C	210^{o}C- 220^{o}C

Results of hot stage microscopy have offered physical evidences for commencement of decomposition, as revealed by contraction of matrix and evolution of gases. Zr based composition in HTPB matrix commenced producing gases in temperature region of 150^{o}C - 160^{o}C. Decomposition of matrix occurred between 210^{o}C- 220^{o}C. In case of Zr based composition in NC-NG matrix, commencement of decomposition was observed in the temperature rate 100^{o}C -120^{o}C. Incorporation of low molecular weight GAP as energetic plasticizer resulted in further reduction in decomposition temperature.

5.3. SEM (Scanning electron microscopy) studies

SEM photographs of Zr based compositions indicated expansion of metal particles at propellant surface during decomposition/ combustion. A significant observation was the diffusion of Zr metal out of oxide skin along with the onset of the decomposition of the binder. This is in contrast to our earlier observation on aluminized fuel rich propellants, where unreacted Al particles were observed on the propellant surface in the form of accumulates due to metal particles concentration. In subsequent stages, an efficient and vigorous combustion of Zr based propellant was observed and formation of deep concave regression on the entire propellant surface was noticed.

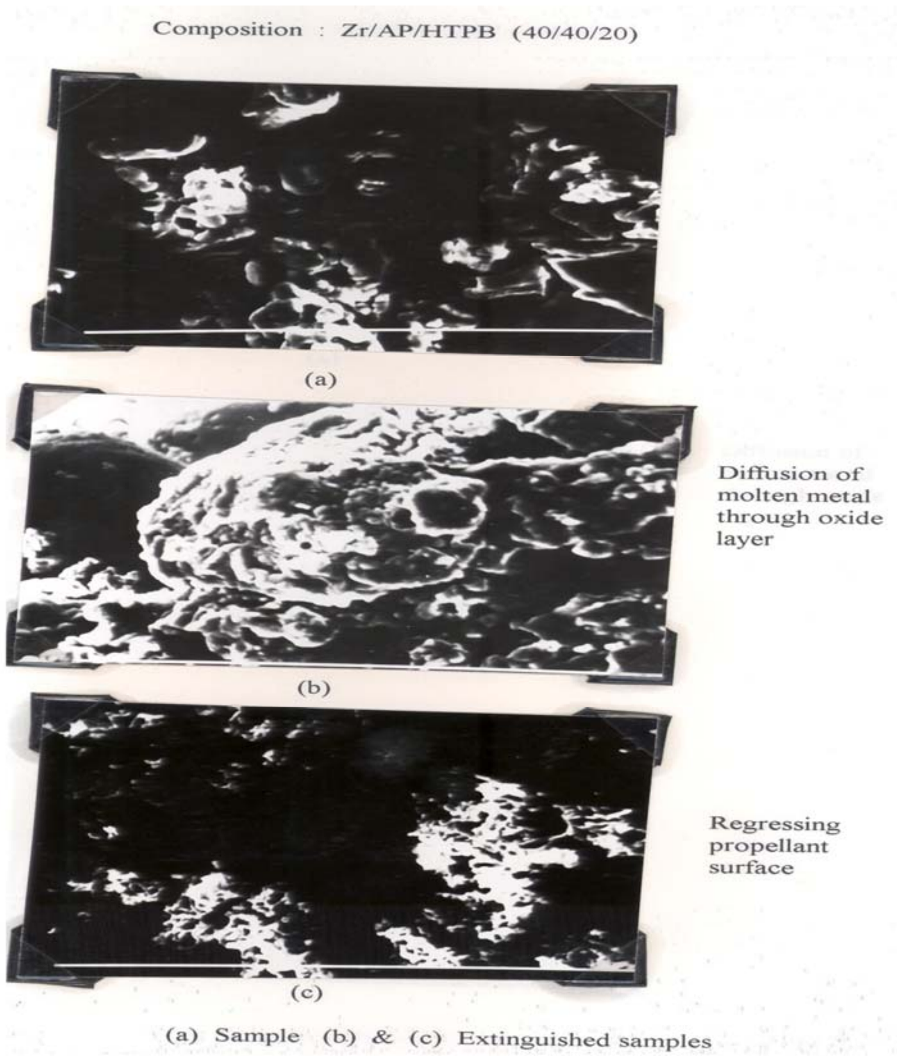
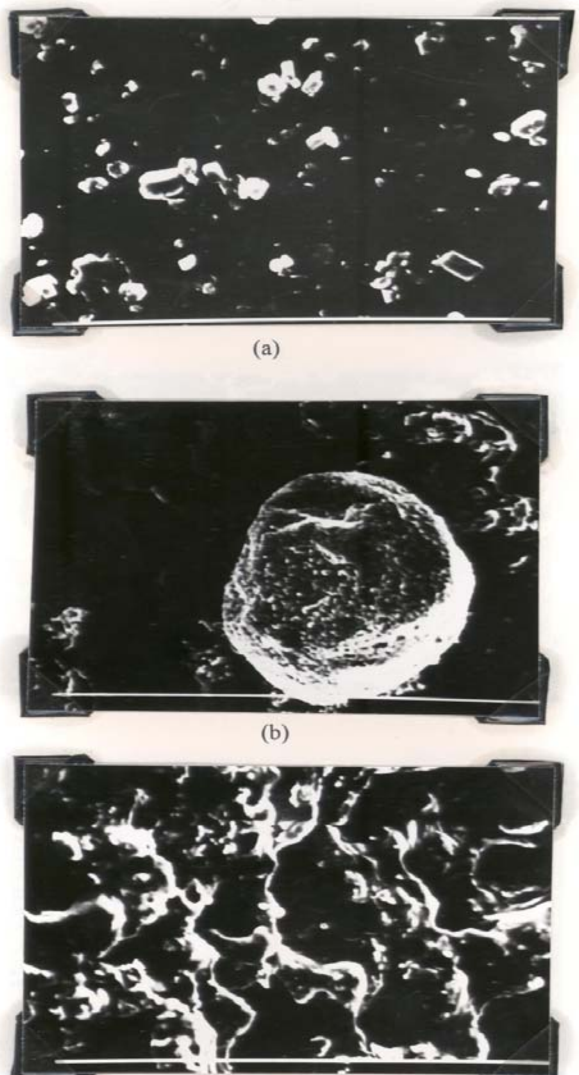


Fig. 6- SEM photographs of FRPs containing Zr-AP-HTPB.

Composition : Zr/AP/DNC/CL (with GAP) (30/10/30/30)



(a)

Diffusion of molten metal through oxide layer

(b)

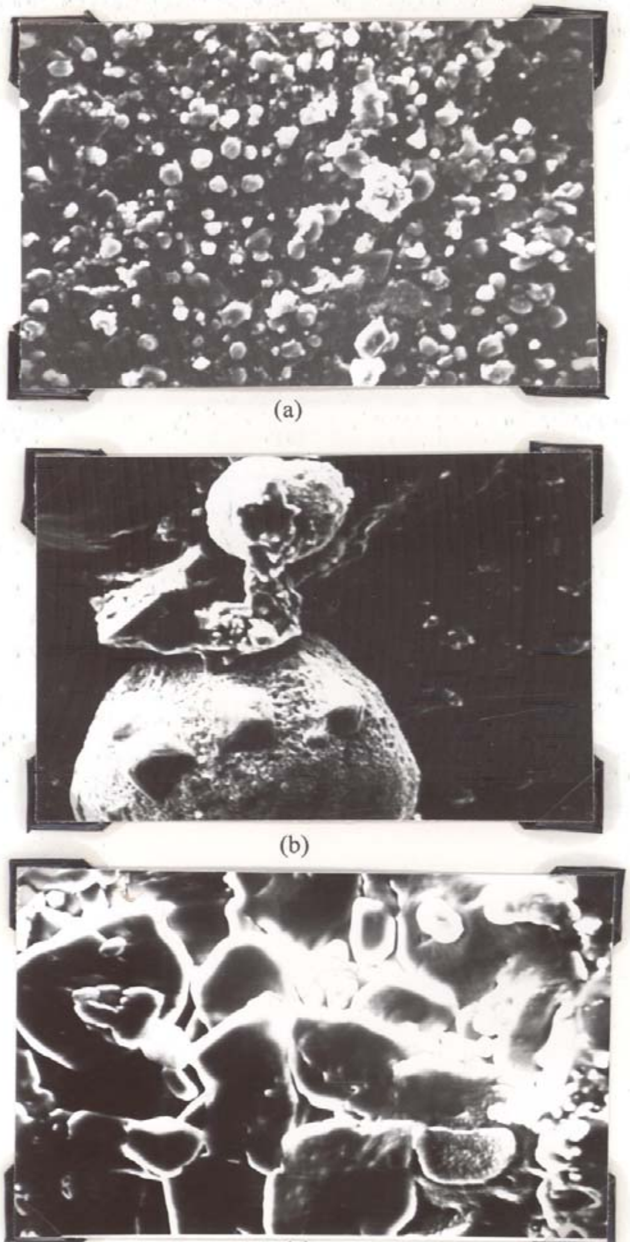
Regressing propellant surface

(c)

(a) Sample (b) & (c) Extinguished samples

Fig. 7- SEM photographs of FRPs containing Zr-AP-NC-NG with GAP.

omposition : Zr/AP/DNC/CL (30/10/30/30)



(a)

(b)

Diffusion of molten metal through oxide layer

(c)

Regressing propellant surface

(a) Sample (b) & (c) Extinguished samples

Fig. 8- SEM photographs of FRPs containing Zr-AP-NC-NG

6. Combustion mechanism

It has been reported that the combustion flame of NC-NG matrix comprises of foam, fizz, dark and luminous zones. The thickness of these zones depends on the pressure level. However, inclusion of AP in NC-NG matrix luminous flame stream comes closer to the burning surface and dark zone gets eliminated. The number of flame streams increased with the increase in concentration of AP until the dark zones is completely eliminated (fig-5).

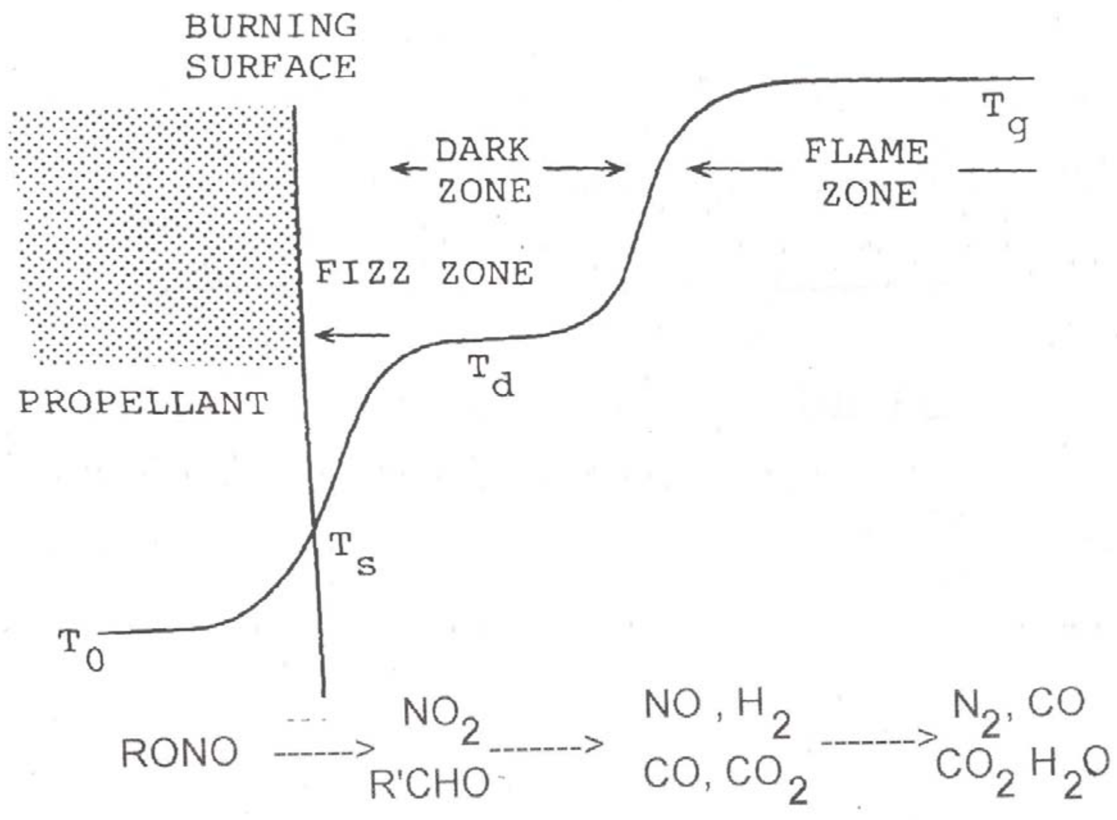


Fig-9: Schematic description of the flame structure of a double based propellant

Flame structure of AP based double base propellants is shown in Fig-6.

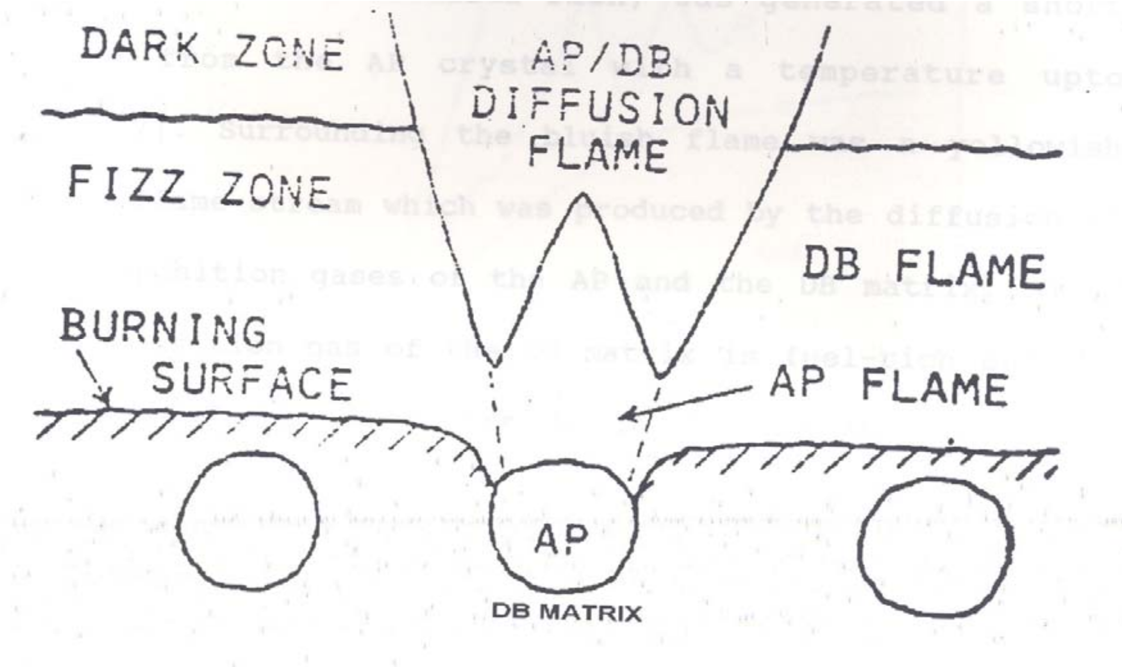


Fig-10: Schematic representation of flame structure of AP based CMDB propellant

In case of double base propellants, since decomposition of NC-NG matrix is fuel rich and temperature in the dark zone is around 1200C, it is possible that diffusion between products of AP and double base matrix leads to shift in equivalence ration towards stoichiometric ratio, resulting in increased reaction rate and higher flame temperature. As a result temperature gradient of AP-double base propellant is higher that of double base matrix. With increase in concentration of AP and reduction in particle size of AP, time averaged temperature gradient in the fizz zone increases. This means higher feedback from gas phase to the burning surface. Consequently burn rates increases significantly.

In case of Zr based fuel rich propellants, unlike Al, oxides of Zr and Ti are soluble in molten metal and both these metals have moderate ignition temperature. These characteristics are responsible for sustained combustion of Zr containing fuel rich propellants. Ni possesses high reactivity and has much higher density than Zr and Boron and therefore appears to be a promising candidate to provide high combustion efficiency to FRPs. Thus, comparatively lower combustion efficiency of aluminized propellants with high metal contents can be attributed to the fact that aluminium oxide serves as an effective barrier for mass diffusion and energy transfer. Moreover, heat sink effect becomes more predominant at high metal content of propellant formulation. Zr , on the other hand, gets easily ignited at around 900^{o}C , which is very close to the burning surface temperature of AP based propellants. Thus, it appears that exothermic decomposition and combustion of Zr results in increase in temperature of the propellants surface due to conductive and radiative heat feedback. Very high burn rates of Zr based fuel rich propellants in double base matrix (2-3 folds) than HTPB based FRPs may be explained on the basis of overall exothermic decomposition of nitrate esters in contrast to endothermic decomposition of HTPB matrix. Comparatively high burn rates with Zr based FRPs as compared to other metals like Al, Mg, Al-Mg alloy could be due to exothermic reaction of Zr oxidation on the propellant surface. Ni has a unique property of reducing the low pressure combustion limit (LPCL) of double base propellants and therefore should be more effective in low pressure region in FRPs containing energetic matrix. Kubota etal. have reported that in case Ni based system, luminous flame generation is observed even up to one bar pressure. They have also reported that flame temperature of double base composition does not exceed 950^{o}C, wereas the same for Ni based FRPs in double base matrix reaches to 1700^{o}C. Incorporation of low molecular GAP as energetic plasticizers in place of di ethyl phthalate (DEP) in double base matrix results in further enhancement of burn rates. These observations are in agreements with the findings of Kubota etal. Higher burn rates of GAP based FRPs may be attribute to the fact that GAP decomposes exothermally at propellants surface with cleavage of N_3 bond, resulting in liberation higher energy of the order of 170 Kcal/mole, leading to efficient combustion. SEM photographs of Zr based FRPs in double base matrix show an efficient combustion of propellant, as revealed by the absence of the formation of deep concave depressions on the propellant surface.

Oxidation of zirconium has been studied for quite some time on solid metal surface, essentially for nuclear applications. Metal powder oxidation will be much faster and highly exothermic due to more surface area available and also due to exothermic decomposition of zirconium with air or oxygen. High temperature oxidation of zirconium in oxygen has indicated that reaction between Zr and oxygen results in dissolution of oxygen in metal and formation of ZrO takes place. Oxidation of Zr is logarithmic below 300 – 400 ^{o}C, which means weight increases with time and temperature. However, above 1000 ^{o}C, only parabolic behaviour has been reported. Above 600^{o}C, dissolution is governed by diffusion in Zr (39-40).

ZrO_2 exist in three modifications namely, monoclinic (below 1000 – 1200^{o}C), tetragonal at higher temperature and cubic above 1500^{o}C. At temperature below 600^{o}C, non-lattice diffusion may be responsible for cubic behaviour. It has been reported that after initial protective oxidation, Zr begins to oxidize at an accelerated rate. Diffusion through the oxide is proposed to take place along the preferred paths. Zr reacts rapidly at 800^{o}C to form zirconium nitride. ZrO_2, ZrN and ZrO are stable up to1500C. Zr removes gases like O_2, N_2, CO, CO_2, and H_2O at 1000^{o}C. In case of Ti, TiO_2, TiN and TiC are stable up to transition point. Energy of activation for oxidation reaction has been found to be 18.2 K.Cal / mol for Zr in the temp range of 200 – 425 ^{o}C, which is lower for Zr oxidation than Ti. For Ti oxidation governing mechanism is diffusion of nitrogen into metals in presence of a thin but permeable nitride film. Higher oxidation rate of Zr in air can be explained, if it is assumed that nitrogen dissolves in ZrO_2. Since nitrogen is quadri -valent, it would create defects in oxygen ion structure, permitting higher rate of diffusion of oxygen through ZrO_2 (41). A similar suggestion has been made by Wagner etal (53). According to these authors three oxides Zr_2O, ZrO and Zr_2O_3 along with ZrO_2 are formed on Zr surface. As compared to Ti, Zr dissolves larger amount of oxygen (42).

While studying metal combustion in explosives and propellants, Halma (43) observed that Al starts igniting at 2200 – 2300 K. Mg evaporates easily and melts at low temp. It was found that burn rate coefficient of Mg – Al was smaller than that of pure Mg or pure Al. It appears Mg – Al alloy based propellants are easily ignitable. Combustion rate coefficient of Zr is of the same order as these of Al and Mg powder based propellants and burn rate coefficient is dependent on specific surface area. Zr and Ti are expected to behave like Mg and Al, as both metals are non-volatile in temp. range involved in combustion and both do not firm protective oxide coating.

Gany etal (44) are of the opinion that condensed phase reactions and processes occurring at fuel grain surface have major affect on over all combustion characteristics of boron fuelled SFRJ. Metal loads of more than 30% may alter gas phase combustion reactions. Gas phase diffusion flame is likely to be less intense than pure hydrocarbon fuel, thus playing less significant role in overall combustion process and heat feedback mechanism .Glowing zones near propellant surface may be the site of special surface activity including sporadic ejection of hot metal particles in various directions.

If melting point of metal is in temperature range of burning surface of propellant, particle coalescence is possible. Concurrent fractures of oxides skins and flow of metal during coalescence results in an increased oxidation rate and ignition. Wherever melting point of oxide is greater than metal, metal oxide may dissolve in molten metal, as in the case of Zr. However, if oxide melting temp. is attained at propellant burning surface, oxide may cause particles to stick together as in case of boron. With high solubility of molten oxide in molten metal (Zr/ Ti), burning proceeds by diffusion of metal to the surface through oxide layer. However, due to low solubility of oxide and low interfacial surface tension between the oxide and metal (Al) oxide tends to accumulate on the surface and interact and exposes the metal. Both Zr and Ti oxides dissolve in metal, resulting in surface reaction and large oxide product particle (45). It appears that in case of Zr, luminous combustion leads to enhanced heat transfer by radiation and hence enhances burn rates. Some metallic elements yield much higher specific heat values as compared to hydrocarbons and hydrogen and specific thrust of different fuels is proportional to square root of specific heat values. Zirconium is a fuel, which demonstrates remarkably high specific thrust as Gany (29) has shown that specific thrust of a ramjet using Zr as a fuel at different flight numbers at sea level will be of the order of 2250 (Mach No 3) and 2500 (Mach No 4) at equivalence ratio of 1.4. These results are in close agreement with our results (32). Reactions of Zr with air produce ZrO, ZrN in addition to ZrO_2. This provides additional energy to the system. Superfine Ti and Zr powder show remarkably higher ignitability and both have high volumetric heat of combustion, much higher than Mg. (46).

Thus, there is tremendous scope for R&D work on Zr, Ti and Ni based fuel rich propellants for ramjet applications. In addition to propulsion of projectiles, one can foresee an emerging trend for change in missile mission implying ramjet propulsion including SFRJ (Solid fuel ramjet propulsion). The demand for longer range flight without increase in the missile size results in the need for more energetic propulsion system. Ramjets are capable of producing much larger total impulse for the same amount of fuel and hence, SFRJ may be considered for missile applications like surface to air, air to surface and most importantly air to air and supersonic cruise missiles.

7. Theoretical performance prediction

Theoretical Isp and density×Isp impulse has been predicted using the equations,

$$I_{sp,\ r} = F/m$$

Where, $I_{sp,\ r}$ = Specific impulse of primary chamber

$$F = mu_e + (P_e\text{-}P_a)\ A_e$$

Where, u_e = exit velocity, P_e = exit pressure

P_a = atmospheric pressure, A_e = throat area

For secondary chamber,

$$I_{sp,\ r\ r} = (a/f + 1)\ I_{sp},\ r\ \text{--}\ (a/f)\ V_a/g$$

Where, $I_{sp,\ r\ r}$ = specific impulse of ram rocket

V_a = velocity of air, a/f = air to fuel ratio

In all these calculations Mach no. 2 was maintained. Results are given in Table-12, 13, 14,15 and16.

Table-12: Theoretical specific impulse of FRPs containing Zr powder in double base matrix.

Zr- 20-40 %, AP- 0- 20 %, NC- 30%, NG (CL) - 30%

Metal fuel Zr (%)	Specific impulse (Isp) at a/f ratio (s)														
	2	3	4	5	6	7	8	10	12	15	20	25	30	40	50
20	345	378	401	418	430	439	445	450	449	440	--	--	--	--	--
30	359	400	427	447	463	474	482	492	495	491	468	--	--	--	--
40	367	419	451	474	492	507	518	531	538	570	522	492	--	--	--

Table-13: Theoretical density- specific impulse of FRPs.

Zr- 20-40 %, AP -0- 20 %, NC- 30%, NG (CL) - 30%

Metal fuel Zr (%)	Density specific impulse (Isp) at a/f ratio ($Kg\text{-}s/m^3$)														
	2	3	4	5	6	7	8	10	12	15	20	25	30	40	50
20	904	990	1051	1095	1127	1150	1166	1179	1176	1153	--	--	--	--	--
30	1102	1228	1311	1372	1421	1455	1480	1510	1520	1507	1437	--	--	--	--
40	1292	1475	1588	1668	1731	1784	1823	1869	1894	2006	1837	1732	--	--	--

Table-14: Theoretical specific impulse of double base formulations

Zr- 20-40 %, AP -0 – 20 %, NC -30%, NG (CL) - 30% (with 8% GAP)

Metal fuel Zr (%)	Specific impulse (Isp) at a/f ratio (s)														
	2	3	4	5	6	7	8	10	12	15	20	25	30	40	50
20	332	362	382	397	407	414	418	421	418	406	375	334	287	186	79
30	345	387	409	427	441	451	457	465	465	458	431	395	351	253	144
40	360	405	434	456	473	485	494	505	510	507	486	454	413	321	222

Table-15: Theoretical density specific impulse of double base formulations

Zr- 20-40 %, AP -0 – 20 %, NC-30%, NG (CL)-30% (with 8% GAP)

Metal fuel Zr (%)	Density specific impulse (Isp) at a/f ratio ($Kg\text{-}s/m^3$)														
	2	3	4	5	6	7	8	10	12	15	20	25	30	40	50
20	873	952	1005	1044	1070	1089	1099	1107	1099	1068	986	878	755	489	208
30	1063	1186	1260	1315	1358	1389	1407	1432	1432	1411	1327	1217	1081	779	444
40	1271	1430	1532	1610	1670	1712	1744	1783	1800	1790	1716	1603	1458	1133	784

Table-16: Theoretical calculations of specific impulse (Isp) at different a/f ratios

Zr-20-60 %, AP -20-60%, binder (HTPB) 20%.

Metal fuel Zr (%)	specific impulse (Isp) at a/f ratio (s)														
	2	3	4	5	6	7	8	10	12	15	20	25	30	40	50
20	368	416	445	466	482	494	504	516	521	520	501	--	--	--	--
30	366	435	468	492	511	527	538	555	563	566	553	--	--	--	--
40	363	449	489	517	439	557	571	591	603	610	603	--	--	--	--
50	359	455	508	540	565	585	602	626	642	653	652	634	606	529	438
60	356	454	525	561	590	612	631	659	679	695	700	686	661	591	501

Above results are self explanatory. In case of 20-40 % Zr based compositions; Isp values were 450, 495 and 570 Sec at air to fuel ratios of 10-15. In terms of volumetric impulse, Zr based compositions have high potential and are much superior as Isp values lies in the range of 904-2006 Kgs/m^3. These results bring out very high potential of Zr as a component of FRPs for futuristic applications. However, detailed studies are needed to tailor Zr based FRPs for practical applications. Thus, Zr alone or in combination with other metal fuel like B, Mg-Al alloy, Ti and Ni can be used to achieve superior performance.

Based on the above logic, Ni based FRPs may be another attractive candidates for futuristic propulsion systems, as they produce stable combustion at low pressures and have higher density(8.9g/cc) and could prove to be an asset for volume restricted system.

8. Summary/ Conclusion

1) Zirconium based fuel rich propellants are very useful for ramjet and scramjet applications and for propulsion of hypersonic cruise vehicles, hyper velocity missiles and air breathing boosters for space applications.

2) Inclusion of 30-70% Zr in propellant formulations produces stable burning rates. 70% Zr based propellant in HTPB matrix gives burning rates comparable with that of 20% Zr based propellant composition.

3) The propellant energy in terms of partial heat of combustion increases considerably with higher percentage of Zr. The density of the propellant increases from 1.8-2.95 g/cc, with increase in Zr content. This makes these propellants very attractive for volume restricted systems.

4) It is possible to load maximum 75% Zr in HTPB based propellants and up to 65% Zr in NC- NG system due to high viscosity build up of the propellant slurry, which is not castable in mould or rocket motor.

5) 20-40% Zr in NC-NG matrix produces very high burn rates and sustained combustion and it is possible to obtained burn rates varying between 12 mm/sec and 19 mm/sec in 5-9 MPa pressure range. Moreover, tensile strength (TS) of propellant increased from 20 Kg/cm^2 to 77 Kg/cm^2 with 40% Zr.

6) Results of hot stage microscopy indicate evolution of gases in the temperature range of 150-160 ^oC for HTPB based formulations, whereas evolution of gases was observed in the temperature range of 100-110 ^oC. Decomposition of propellant matrix takes place in the temperature range of 210-220 for both HTPB and NC-NG based propellants.

7) SEM studies indicate expansion of metal particles at propellant surface during decomposition and combustion. Unlike aluminised propellants, in Zr based propellants diffusion of Zr metal particles takes place and Zr oxides are soluble in propellant matrix.

8) Zr based propellant compositions produce high volumetric impulse and Isp of the order of 900 - 2000 Kgs/m^3 can be obtained.

9) Suggestion/ recommendation I

1- Zr based fuel rich propellants are very attractive for volume restricted systems and must be considered as a potential candidates for air to air and air to surface missile applications.

2-- Based on the data generated in the present study on Zr based fuel rich propellants, and on the basis of similarity in properties of Zr, Ti and Ni, there is tremendous scope for research work on Ti and Ni based fuel rich propellants, as they are capable of producing higher specific thrust and their densities are very attractive (8.9 g/cc for Ni). Further, Ni produces stable combustion even at very low pressures of 10 Kg/Cm^2.

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Appendix- A
Personal supported:

1) Himanshu Shekhar- Scientist

2) Samrat Wavhal- Project Assistant

3) Ravikant Balakshe- Project Assistant

4) MS Seema Rai- Consultant.

5) MS Savita Kumar – Consultant.

Appendix- B
Publications:

1) Current trend of R&D in the field of Zirconium based Fuel Rich Propellants (FRPs) for Ramjet applications. Journal of Defence science, New Delhi. (Communicated).

2) Studies on Zirconium based Fuel Rich Propellants.

Sudhir Avachat*, Reuben Daniel* and Haridwar Singh**

Presented during 7th International conference on high energy materials. Dec 8-10 2009, HEMRL, Pune, India.

Accepted for publication in the International Journal Aerospace Engineering, after review by referees.

3) Studies on Zirconium based fuel rich propellants for ramjet and scramjet applications.
Accepted for presentation during International workshop- HEMs-2010 (High energy materials demilitarization and civil applications) 8- 10 Sept. 2010, FRPC, Altai, Biysk, Russia.

Appendix - C

1) Int. workshop on processing of composite propellants. HEMRL, Pune, Oct 18-20 (2008).
2) National conference on High Explosives Technology, T.B.R.L. Chandigarh, Nov 2008.

3) International Conference on Armaments, A.R.D.E. Pune, India, Nov 2008.

4) 8th Int. conference on high energy materials & special topics in chemical propulsion. 2-7, Nov 2009. South Africa.

5) 7th Int. conference on High energy materials, HEMRL, Pune 8-10 Dec 2009.

6) One day conference on Synthesis of HEMs. 30th Jan' 2010, University of Hyderabad, India.

7) International workshop on high energy materials- Demilitarization and civil applications, 8-10 Sept. 2010.

8) Discussion with Prof Alon Gany, Faculty of aerospace Engg, IIT, Haifa, Israel during June – July 2009.

(Note-P. I. was Visiting Professor at I.I.T. Haifa during June- July 1009.)

Appendix- D

Inventions

1) DD for 882 enclosed

<table>
<tr><th colspan="4">REPORT OF INVENTIONS AND SUBCONTRACTS</th></tr>
<tr><td rowspan="2">1. a. NAME OF CONTRACTOR Dr. HARIDWAR SINGH VISITING PROFESSOR</td><td rowspan="2">c. CONTRACT NUMBER: AOARD-084092 (FA23860814092)</td><td rowspan="2">2.a. NAME OF GOVERNMENT PRIME CONTRACTOR-NA</td><td>3. TYPE OF REPORT: FINAL</td></tr>
<tr><td>4. REPORTING PERIOD</td></tr>
<tr><td rowspan="2">b. ADDRESS: DEFENCE INSTITUTE OF ADVANCE TECHNOLOGY, GIRINAGAR, PUNE-411021</td><td rowspan="2">d. AWARD DATE: 2008/08/08</td><td rowspan="2">b. ADDRESS: NA</td><td>FROM: 2008/08/08</td></tr>
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<tr><td colspan="9">5. “SUBJECT INVENTIONS” REQUIRED TO BE REPORTED BY CONTRACTOR/ SUBCONTRACTOR</td></tr>
<tr><td>NAME OF INVENTOR</td><td>TITLE OF INVENTION</td><td>DISCLOSURE NUMBER PATENT APPLICATION SERIAL NUMBER OR PATENT NUMBER</td><td colspan="4">ELECTION TO FILE PATENT APPLICATION</td><td colspan="2">CONFORMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER</td></tr>
<tr><td rowspan="2">Prof. Dr. SINGH HARIDWAR</td><td rowspan="2">“High burn rate Zirconium based fuel rich propellants for ramjet applications”.</td><td rowspan="2">TOBE FILED</td><td colspan="2">U.S.</td><td colspan="2">FOREIGN</td><td rowspan="2">YES</td><td rowspan="2">NO</td></tr>
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SECTION-2 SUB CONTRACTS AND SECTION-3- CERTIFICATION IS NOT APPLICABLE IN PRESENT CASE.

Appendix- F

Reprints of the papers are enclosed-

1) Current trend of R&D in the field of Zirconium based Fuel Rich Propellants (FRPs) for Ramjet applications.

HARIDWAR SINGH
Visiting Professor,
D.I.A.T. (DU), Girinagar, Pune (India).

ABSTRACT

Rocket ramjet offers higher propulsion efficiency than solid rocket propellants. Major advantages of ram rockets include reduced missile weight, higher density and higher volumetric energy. Al, Mg, B and Zr metal powders have found application as fuel rich propellant (FRP) ingredient for ramjet/scramjet applications. FRPs generally contain high metallic fuel, polymeric binder cum fuel and minimum quantity of oxidizer or preferably no oxidizer. Currently, there is renewed interest in ramjet propulsion for futuristic supersonic flight missions and hypersonic cruise missiles, hypervelocity missiles and air breathing boosters for space applications. Since most of the literature on Zirconium (Zr) based propellants is scattered, patented or classified, an attempt has been made in this manuscript to review R&D work specifically with respect to Zr based fuel rich propellants, in view of their tremendous advantages for volume restricted propulsion systems. This paper covers back ground

information, important properties of ingredients, processing technologies and review of current R&D work carried out in the field of Zr based fuel rich propellants. Our recent findings have indicated that it is possible to achieve very high burn rates using 40% - 60% Zr powder in NC-NG matrix along with very high density of 2.25 g/cc. This paper also covers the results of combustion studies of metalized FRPS based on both conventional binders and energetic binders like GAP and BAMO. It is predicted that specific thrust of a rocket ramjet using Zr as fuel will be around 2050 at Mach no. 3 and 2500 at Mach no. 4. Oxidation reactions of Zr produce ZrO, ZrN and ZrO_2, which provides additional energy to the propellant system.
Key words- Fuel rich propellants, zirconium based propellants, ram rockets, Integrated rocket ramjet, advanced propellants.

1. Background and motivation

Hypersonic air breathing propulsion has been on the minds of human kind for a very long time. Solid propellant ram rocket (SPR), known as ducted rocket or air breathing propulsion systems belong to ramjet family. In 1913, Renelorn of France was first to recognize the possibility of using ram pressure in a propulsion device. Albert Fono of Hungary was granted a German patent in 1928 on a propulsion device that contained all elements of a modern ramjet and was intended for supersonic flight. During 1950s and 60s, efforts were made in USA and Germany to investigate this powerful propulsion system. In Russia (then USSR), SPR development was carried out, leading to application of IRR (Integrated Rocket Ramjet) propulsion for SAM-6 anti-aircraft missile. This became operational during 1967. Amongst the other operational missiles, propelled by ramjet are American Bomarc (1957) and British Blood hound (1959), followed by others during 1970's (1-3). There were not many R&D activities during the period 1970s and 80s, although ONERA, France demonstrated SPR propulsion system during 1976 and MBB Germany in 1981.The basic design of SPR is given in Fig. 1.1.

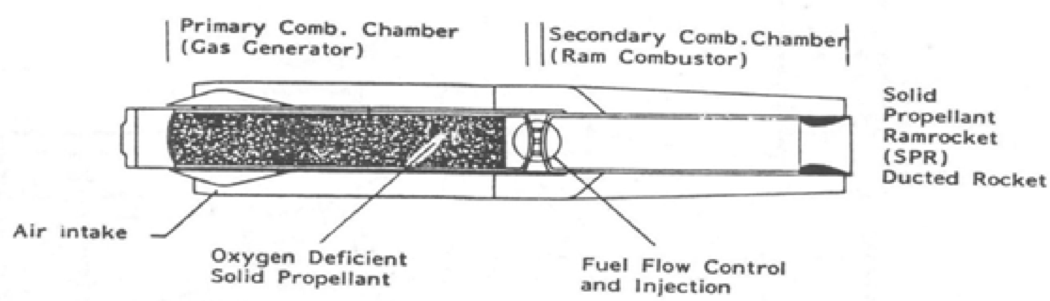

Fig. 1.1: Basic design of SPR

In SPR an oxygen deficient solid propellant called as a fuel rich propellant (FRP) burns in the primary combustion chamber as gas generator propellant. Fuel rich combustion products of primary chamber are passed through the secondary combustion chamber, known as ram combustor, where they mix and burn with ram air supplied by the air intake system. Since atmospheric air is used in SPR for full combustion, the incorporation of solid oxidizer in propellant reduces the energy in terms of specific impulse (Isp). SPR permits inclusion of high

proportion of energetic ingredients such as oxidizers and metallic fuels like Al, Mg, B, C, Zr etc. in the propellant composition. The high temperature of combustible products injected in the ram combustion allows high combustion efficiency and eliminates additional device to initiate the ignition during ram rocket combustion. Thus, the major advantages of ram rockets include reduced missile weight (as oxidizer is not carried along with propellant) as compared to conventional solid rockets.High density materials incorporated in FRPs produce high volumetric energy due to higher heat of reaction with oxygen and improvement in the propellant density.   Currently, there is renewed interest in ramjet propulsion for futuristic supersonic flight missions like Cruise missiles for air to air applications and other defense missile systems. Ramjet appears to be the most efficient solution for these missions. European long range air to air missile, Meteor, propelled by a ducted rocket engine is one of such examples. Ramjet propulsion provides efficient operation along with very high specific thrust to overcome drag. In the field of gun launched ramjet projectiles, SFRJ (solid fuel rocket ramjet) is highly promising propulsion system. Supersonic muzzle velocity provides operating conditions for ramjet propulsion.

Possible applications for scramjet include hypersonic cruise vehicles, hypervelocity missiles and air breathing boosters for space applications. For hypersonic missiles, air breathing system operating below Mach 6, using hydrocarbon fuels are preferred, in view of volumetric and operational constraints. One of the very attractive missions identified for scramjet powered propulsion vehicle is the Mach 8 cruise missile as standoff fast reaction weapon or a long cruise missile. Typically, in IRR propulsion booster rocket provides a high thrust for short duration, followed by sustained thrust for long duration in sustainer phase. All modern ramjet missiles use IRR concept, where combustion of high energy solid propellants (composite or composite modified double base propellant) provides high thrust in boost phase. Subsequently, ramjet mode starts the nozzle and ramjet power begins. Basic ramjet engine consists of an inlet, diffuser, combustion chamber and exhaust nozzle (Fig-2)

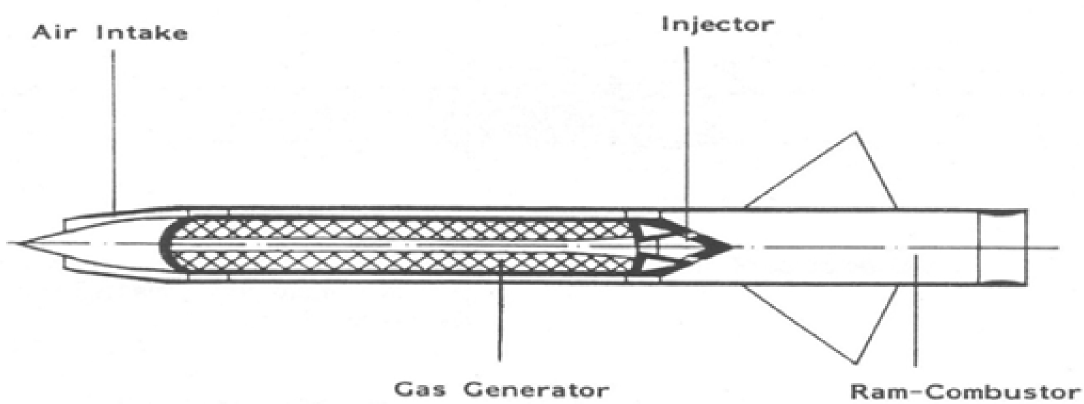

Fig-2 Basic ramjet engine

The unique combination of heat addition in supersonic air stream with variable shock system and absence of a geometric throat permits a scramjet to operate efficiently over a wide range of flight conditions. This means a nozzle subsonic combustion ramjet at low flight mach number (M=3-6) and a supersonic combustion ramjet at high mach number (M>5). The performance of an air breathing engine is always higher than that of a rocket and by using scramjet this advantage can be extended to a higher Mach region. Since, most of the literature on zirconium based solid fuel rocket ramjet is scattered, patented, classified and has not been reviewed, and keeping in view of their tremendous potential to offer very high specific thrust, an attempt has been made in this paper to cover R&D work done so far and discuss important features of metallised FRPs in general and Zr based FRPs in particular including their combustion behaviour.

2. Important historical developments

Fry (4) has given an excellent account of ramjet propulsion technology evolution covering first to fourth generation scramjet development. During late1990s, NASA established long range goals for exploration of space. Third generation launch system of NASA is expected to be fully re-usable and should be operational by 2025. The main objective of this launch system is to reduce cost of launch by a factor of 100 and improve safety by a factor of 10,000 over current propulsion devices. Recently, many international joint R&D activities have commenced. A joint French-Russian research programme for wide range of ramjet has been initiated to develop technology for re-usable space launchers. Another French effort, leading to high speed dual mode ramjet propelled vehicle at mach 4-8 is expected during the period 2010-2012. Japanese national aerospace laboratory has commenced design, fabrication and testing of a side wall compression type scramjet engine (5-12).

It is apparent from above account that scramjet development has come of age during 1990-2000, with good understanding of the technology that will enable ramjet powered flights in future. Thus, scramjet technology developments are underway in many countries of the globe to capitalize on pay offs that hypersonic speeds and long range can provide. U.S. Navy has initiated a programme in 2002 to demonstrate ramjet propulsion technology to enable hypersonic long range missiles.

3. Important properties of ingredient used in fuel rich propellants (FRPs)

Major ingredients used in FRPs include an oxidizer, a binder cum fuel, metallic fuel, burn rate catalysts and additives to impart suitable properties to the propellant composition. Important properties of these ingredients, although mentioned at various places in scattered way have been included in this paper for ready reference.

3.1. Oxidizers:

The oxidizer selected for FRPs must produce high gas output to achieve high expulsion efficiency from the gas generator propellant. Higher gas output reduces deposits within wall and injector orifice and also minimizes losses in the thrust nozzle due to particle flow. The oxidizer must, therefore, provide high combustion temperature, high oxygen content and high oxygen balance. It should also have high density to minimize oxidizer volume in the propellant and it should produce least exhaust plume, which contributes to the signature of the missile. Generally, reaction products, which cause signature, are metal oxides, metal chlorides and hydrochloric acid and hence oxidizers containing chloride groups are not be preferred. In addition, oxidizer should be compatible with other propellant ingredients. It should have low hazard and minimum risk and low cost. The important oxidizers, which can be used in FRPs, are given in Table-1.

Table-1: Important properties of potential oxidizers.

Oxidizers	Chemical Formula	Reaction Products	Specific Gravity, g/cc	Oxygen Content, %
Nitronium Perchlorate (NP)	NO_2ClO_4	-----	2.22	66.0
Nitrosyl Perchlorate	$NOClO_4$	-----	2.17	61.8
Lithium Perchlorate (LP)	$LiClO_4$	LiCl	2.43	60.1
Ammonium perchlorate (AP)	NH_4ClO_4	N_2, HCl, H_2O	1.95	54.5
Sodium perchlorate (SP)	$NaClO_4$	NaCl	2.54	52.2
Potassium perchlorate (KP)	$KClO_4$	KCl	2.53	46.1
Lithium nitrate LN)	$LiNO_3$	Li_2O	2.38	69.6
Ammonium nitrate (AN)	NH_4NO_3	N_2, H_2O	1.73	60.0
Sodium nitrate (SN)	$NaNO_3$	Na_2O	2.26	56.5
Potassium	KNO_3	K_2O	2.11	47.5

nitrate (KN)				
HMX	$(CH_2N_2O_2)_4$	-----	1.90	43.2
RDX	$(CH_2N_2O_2)_3$	-----	1.70	43.2
Cl-20	-	-----	2.04	+11(0B)
HNF	$NH_2N(NO_2)_3$	-----	1.86	+21.8(0B)
ADN	$NH_4N(NO_2)_2$	-----	1.80	+25.8
Note: HMX= cyclo tetramethylene tetranitramine, RDX= cyclonite(cyclotrimethylene trinitramine) CL-20 = Hexa nitro hexaaza isowurtzatine HNF = Hydrazinium nitro formate AND = Ammonium dinitramide				

In practical formulations developed so far mostly AP, KP, AN, SN and KN have been used as oxidizers. Additives like RDX/HMX and being evaluated to boost energy further. While NP is unstable, LP is highly hygroscopic and not readily available.

Amongst the nitramines, HMX has higher density (1.9 g/cc) and doesn't produce smoky exhaust products. The heating value improves significantly, if AP is replaced partially with HMX. However, HMX based compositions produce lower burn rates and high pressure index values. Use of co-oxidizers will be always advantageous from energy and signature point of view. New oxidizers namely, HNF and ADN are promising, provided they do not create incompatibility problem with binders used and their high friction sensitivity is taken care of by suitable coating. CL-20 can be used as energetic additive.

3.2. Fuels:

Both conventional and energetic polymeric fuels and metallic fuels have been used as major ingredients of FRPs. CTPB (carboxy terminated polybutadiene) and HTPB (hydroxy terminated polybutadiene) have been used extensively and shall remain in use for many years, till new energetic polymeric materials like GAP (glycidyl azide polymer) and BAMO (Bis azido methyl oxetane) become fully operational. Low viscosity of the polymer for higher solid loading, low glass transition temperature (Tg) of the order of -50 C and better mechanical properties will be always preferred to ensure high level of structural integrity of FRPs for various applications (13).

Metallic fuels are incorporated essentially to increase volumetric heating value and also to increase combustion temperature (T_f) to achieve auto- ignition of ram combustion and also to achieve enhanced combustion efficiency in the secondary chamber. Important properties of conventional and energetic fuels (13) along with metallic fuels and energetic plasticizers are given in Table- 2, 3 and 4.

Table-2 Properties of energetic polymeric fuels-

Binders cum fuel	Density (g/cc)	T_g (^oC)	Impact sensitivity (cm)
GAP (Glycidyl azide polymer)	1.3	-50	170
Poly GLYN (Poly glycidyl nitrate)	1.42	-35	200
Poly AMMO (Azido methyl methyl oxetane)	1.06	-35	90
Poly NIMMO (Nitrato methyl methyl oxetane)	1.26	-30	90
Poly BAMO (Bis azido methyl oxetane)	1.30	-45	200
Poly BAMO-THF(Tetra hydro furan)	1.32	-45	210
HTPB (Hydroxyl terminated poly butadiene)	0/93	-50	>200

Table - 3: Important properties of metallic fuels.

Metallic fuel	Specific gravity	At. Wt	Valency	M.P. ^oC	B.P. ^oC
B	2.45	11	3	2300	-
Al	2.70	27	3	660	2450
Mg	1.74	24	2	650	1107
Zr	6.49	91	2,4	1850	4377
Ti	4.5	48	2,4	1675	3260

Ni	8.9	59	2,4	1455	2900
LiH	0.82	8	1	668	720 (decomposes)
MgH_2	1.42	26	2	327 (decomposes)	-
AlH_3	1.5	30	3	150	decomposes
TiH_2	3.9	50	2	400 (decomposes)	-

Table 4: Important properties of selected energetic plasticizers.

Plasticizers	Density (g/cc)	Oxygen balance (%)	Heat of formation (Kg/KJ)	Impact(cm)
TMETN	1.46	-34.6	--	8.8
BTTN	1.52	-16.6	--	4.7
Bu-NENA	1.20	-104	-140	--
BDNPA/F	1.39	-58	-82	96
DEGDN	1.38	-41	--	--
DANPE(1,5 diazido 3,3 nitroazo pentane)	--	-80	554	--
Diethylene glycol bis-azido acetate	1	-100	-392	--
Trimethylol nitro methane	1.4	-72	-230	--

triazido acetate				

Boron is the most favorable energetic metallic fuel, but is difficult to burn under ram combustion conditions. This is due to the reason that high temperature is required to evaporate boron oxide. On the other side, Mg does not provide major improvements from the energetic point of view. However, it can be easily burnt with high efficiency and with increased primary combustion temperature. In view of the above, now priority is being accorded to metallic fuels, which have higher density and whose oxidation and combustion reactions are highly exothermic. In this regard Zr, Ti and Ni appear to be very attractive as their density varies between 4.5 and 8.9 g/cc. Moreover, melting point of these metals is also comparatively lower than boron and their oxides are soluble in molten metal. Another advantage is that their air to fuel ratio lies in the region of 1.5 to 3. Ramjet performance is drastically affected by flight parameters as well as by fuel properties. For volume restricted system, it is the energy density ($\rho \times E$), which indicates the energy contained in a unit volume of fuel.

3.3. Catalysts:

Generally, burn rate catalysts are added to FRPs to obtain required burn rates of oxygen deficient solid propellant systems. Many times catalysts not only increase the burn rate, but also reduce pressure index values and temperature sensitivity coefficient. Various iron/copper based catalysts used include ferrocene, n-butyl ferrocene, catocene, copper chromite etc. Iron oxide has been also used as burn rate catalyst. With the advent of nano materials, there is a wide possibility of their application in development of new class of advanced FRPs of very high burn rates. It is expected that combustion mechanism of FRPs containing nano metric size metallic powder and energetic binders may be entirely different than conventional micron size material.

4. Processing of FRPs:

Well known processing techniques namely, extrusion, pressing and casting can be used to process FRPs. The selection of processing methodology depends upon the type of formulations and ingredients used. For higher solid loading (>90%) FRPs pressing technique is preferred. This involves mixing of ingredients in suitable mixers, followed by pressing in suitable form in mould or motor. This requires high caliber presses of about 1000 Ton or more. In case of casting method, ingredients are mixed in a vertical planetary mixture just like composite propellant processing. Thoroughly mixed ingredients and are then cast under vacuum (3-5 mm of Hg) in mould or rocket motor, followed by curing at elevated temperatures and remote control mandrel extraction. The detailed processing techniques are discussed under reference-14.

5. Current R&D trend on Zr based fuel rich propellants

Most of R&D work on Zr and Ti based FRPs is of recent origin. Although, these fuels are well known and have very high potential due to their higher densities and high volumetric heating values, as compared to other metallic fuels like Al, Mg, etc. Use of other metallic compounds like metal hydrides, metal borides and metal alloys has also been recommended to increase heat content of FRPs. Further, ultrafine Zr powder ignites very easily and burns extremely rapidly producing high heat.

We published a review article on “Metalized FRPs for solid rocket propellants” during 1994. This paper covers the details of various formulations based on different metallic fuels. This article covers most of the R&D work carried out up to 1990 in the field of metalized fuel rich propellants based on Al, Mg, B etc without any specific reference on the type of metal powder used (15). Most of further R&D works in this area are covered in the papers published during the period 2004-2007 as per references given under (16-29). Thomas John has reported results of burning rates of Al, Mg and their alloy based formulations with HTPB as binder and AP as oxidizer. In general, burn rates were lower with increasing metal content. Lower pressure index values were obtained for aluminized formulations containing 45-50% Al. Inclusion of copper chromite as burn rate catalyst increased burn rates by almost 150%. At same oxidizer level, Mg based formulations produce higher burn rates. Invariably, Al-Mg alloy based formulations produce higher burn rates than individual Al or Mg based formulations. This could be due to the reason that Al-Mg alloy has lower ignition temperature and higher burn rates than pure Al and Mg based formulations. Greater reactivity of Al in the combustion process in presence of Mg would be an added advantage. Addition of Al sensitizes thermal decomposition of AP, whereas Mg-Al alloy induce lower ignition temperature by 100^0C. This indicates higher reactivity of AP with Mg-Al alloy (30).

Most of the formulations studied earlier are based on HTPB-Al/Mg/Al-Mg alloy and boron. However, now the trend is to use energetic binders and energetic plasticizers in place of conventional inert binders and inert plasticizers like organic phthalates and acetates. FRP formulations based on poly BAMO and poly NIMMO are capable of giving Isp of the order of 900-1200 sec. Of late, GAP (Glycidyl azide polymer) based fuels are being evaluated for IRR applications. Low molecular weight GAP (500-700) can be used as energetic plasticizer, where as high molecular weight GAP (2500-4000) can be used as energetic binder cum fuel. GAP has another unique advantage of producing self sustaining burning in primary rocket motor without any oxidizer. An important attribute of azide based polymers like GAP and BAMO and their co-polymers is their positive heat of formation, resulting in highly exothermic reactions during decomposition. This can be considered as an added advantage, as butadiene based polymers like HTPB and CTPB decompose in an endothermic mode, thereby giving heat sink effect to propellant combustion. A few formulations based on Zr-AP- GAP have also been studied recently . Inclusion of GAP is reported to enhance burn rates significantly (31).

Lou etal (32) patented a FRP composition with 80-90% of 2-4 micron size Zr and containing 10-20% AP. They have claimed high burn rates and low burn rate sensitivity can be obtained by controlling particle size distribution of Zr. Harry (33) has patented high gas producing FRPs containing up to 40% Zr. Reed et.al. (34) have patented an improved Zr based ramjet fuel using hydroxyl terminated fluorocarbon as binder. Thus, only limited numbers of studies were conducted on Zr based fuel rich propellants for ramjet and scramjet applications and most of earlier literature is covered under patents.

While studying effect of fuel properties on specific thrust of a ramjet engine, Gany et al (28) have analyzed different elements for their maximum potential for maximum specific thrust for volume restricted system and found that for maximum thrust Mg, Al and Zr are most promising. These metals produce three times higher combustion energy per unit mass of air than hydrocarbon fuel. This means possibility of achieving 50% higher maximum specific thrust with a penalty of reducing Isp.

We have reported recently that 20-40% Zr with HTPB as binder and with AP as oxidizer produces stable combustion in 1-9 MPa pressure region. With 20% Zr, burn rates varied between 3.7 mm/sec and 6.7 mm/sec in the pressure range mentioned above, whereas 40% Zr produced burn rates varying between 2.3 mm/s and 5.2 mm/s in same pressure region. The pressure index values of these formulations were around 0.34 and density obtained was 2.03 g/cc for 40% Zr based formulations. NC-NG matrix with 30% Zr produced high burn rates of 6-19 m/sec in the pressure range of 1-9 MPa. Whereas in case of 40% Zr based formulations, burn rates varied between 12 mm/sec and 17 mm/sec in pressure region of 3.1-9 MPa. Cal-val (Partial heat of combustion) of these formulations was in the range of 1000-1200 cal/gm(35). Mechanical properties of NC-NG based FRPs were very high (4-7.7MPa) and percent elongation was around 30%.

Kubota et al (36- 37) have studied the combustion of Zr & Ti particles with KNO_3 and found that while Ti particles react exothermally at 970K with decomposed gases of KNO_3,whereas Zr particles react at 700K with liquefied products of KNO_3. Burning rate of Ti-KNO_3 based formulations was found to be more sensitive to pressure than that of Zr-KNO_3 based formulations. They have suggested that major exothermic reaction in the combustion wave of Zr-KNO_3 takes place in the condensed phase and burn rates are dependent on oxidizer to fuel ratio. Burning rate of Zr-KNO_3 was found to be less dependent on pressure and heat generated by exothermic reaction between Zr particles and gasified KNO_3 with increase in Zr fraction. The activation energy was found to be 105 kJ/mole for Zr-KNO_3 composition, whereas the same for Ti-KNO_3 based formulations was 200 kJ/mole. In addition, moderate ignition temperature of these compositions also helps in producing stable combustion. These results indicate that Zr based compositions decompose at lower temperature than Ti based formulations.

We have also reported comparative effect on ballistic performance of metalized fuel rich propellant and found the 20-40 % Zr based compositions can produce Isp of 570 sec at air to fuel ratio of 15. In terms of density-specific impulse, Zr based compositions are capable of producing very high performance (900-2006 Kg-s/cubic meter × 10^3), followed by Ti based compositions which can produce density-specific impulse of 800-1850 Kg-s/ cubic meter × 10^3. (31) The findings of this studyclerly bring out very high potential of Zr based fuel rich propellant for futuristic applications. Moreover, Zr can be used alone as metallic fuel as well as in combination with other metal fuel to achieve superior combustion efficiency. (38).These results indicate that Zr based formulations are very attractive and highly promising for both ramjet and scramjet applications, particularly where designer has the constraint of restricted volume. However, detailed and exhaustive studies on formulation, processing and evaluation including their thermal decomposition and combustion behavior are needs. In addition, behavior of nano sized Zr powder along with their sensitivity data is required to be studied in great detail, before these compositions can be adopted for practical applications.

6. Combustion studies of metalized fuel rich propellants:

The basic metal combustion process is not expected to change significantly in propellant formulation including air breathing ram rockets, although combustion behavior of metals is influenced by their thermo-chemical characteristics as well as physical properties like coefficient of thermal expansion and solubility of metal oxides. A number of studies have been carried out in past on the combustion of metals (38-41). Metals like Al form agglomerates at the propellant surface due to lower burn rates of FRPs. It has been found that agglomeration diminishes, if metal ignition takes place rapidly on the exposure to combustion gases and oxygen rich flame is situated closer to the burning surface. It is reported that oxidizer-binder decomposition and interaction produces non-equilibrium combustion temperature, which decides whether metal will melt or ignite. However, replacement of binder by metal powder increases non-equilibrium combustion temperature. In case of aluminized FRPs, small Al particles fill the space among the larger oxidizer particles and each particle experiences temperature rise as it approaches the propellant surface. Wood (42) found that particle size of metal plays an important role in combustion, as 5 micron Al particles get ignited at the propellant surface. Vernekar et al (43) found that in pressed AP-Al pellets, maximum burn rate is obtained at intermediate metal content. Jain et al (44) investigated thermal ignition behavior of Mg in a mixture containing Al along with organic fuels and found that a FRP composition containing Mg ignites at lower temperature.(<145^{o}C), when mixed with organic fuel. Among other metals Ni, Sn, Zr etc appear to be closer to Mg. Lilijagren et al (45) have reported that Mg up to 50% in FRP containing about 30% AP should produce stable combustion in presence of catalysts like iron oxide. Mg-$NaNO_3$-napthlene based compositions have been evaluated in many countries due to their self paralyzing property. It has been found that fuel richness leads to improvement in ballistic performance.

In case of boron based formulations, four reaction zones have been identified. These include inert heating zone, sub-surface reaction zone, first stage combustion zone and second stage combustion zone. When boron content is less than 20%, boron and B_2O_3 particles can reach second stage ignition temperature of 2000K and sufficiently higher amount of heat is released due to efficient combustion of boron. However, when boron content exceeds more than 20%, energy sink effect becomes a dominant factor in reducing heat feedback to the burning surface. Murphy (46) has suggested that the conductive, convective and radiative heat transfer between boron based propellant ingredients and their combustion products contribute significantly. They have found that boron burns only if particle size is extremely small or combustion temperature is very high. Kubota et al (47) have studied FRPs with boron content of 20-40% along with AP in CTPB binder and found an increase in Isp with increase in B content as well as increase in air to fuel ratio. Theoretical Isp for a composition containing 40% boron has been calculated as 1400 seconds.

Gany et al (48) studied combustion pattern of propellant containing 40-50% of metal additives by using high speed photography in conjunction with high pressure window strand burner. They found that the propellant combustion was irregular and regression rate varied from 0.3 to 3 times the average value in case of boron based system. Gany et al (49) have also reported combustion behavior of highly metalized solid fuels and found existence of gas phase diffusion flame of the volatile fuel ingredients within the boundary layers above the fuel surface. Material is emitted from the surface in the form of large pieces and segments. This promotes high speed ejection of hot particles and disintegration of large glowing segments and pieces from the fuel surface layer into the gas stream. Thus, surface zones are the site of surface activity responsible for shooting of particles at high speed into the gas stream. Kuo et al (50-51) have studied ignition and combustion characteristics of boron based solid fuel and found that metal powder reduces the ignition delay of poly BAMO and NIMMO based compositions significantly. It was found that boron particles affect the fluid dynamics of the gaseous jet. It also helps in increasing absorption in the gas phase. The combined result of these two effects is the significant reduction in ignition delay time.

While studying ignition and flammability characteristics of SFRJ, it has been found that presence of carbon black in the formulation improves the ignition and flammability limits more effectively than addition of 5% combustion catalyst. Inclusion of carbon black in the fuel results in radiative heat transfer from the flame being adsorbed at the surface rather than providing self-surface heating. While studying temperature effect on SFRJ fuel properties and combustion, it has been reported that the presence of combustion catalyst results in reduction of the temperature at which exothermic reactions occur. Combustion of metallic fuel or hydrocarbon is essentially oxidation and reduction reaction. Fuel rich species get oxidized, whereas oxidizer is reduced to form decomposition products, which further react with decomposition species and reaction proceeds further till stable products like CO_2, H_2O, CO, H_2, metal oxides etc are formed and reactions are complete in all respects.

Oxidation of zirconium has been studied for quite some time on solid metal surface, essentially for nuclear applications. Metal powder oxidation will be much faster and highly exothermic due to more surface area available and also due to exothermic decomposition of zirconium with air or oxygen. High temperature oxidation of zirconium in oxygen has indicated that reaction between Zr and oxygen results in dissolution of oxygen in metal and formation of ZrO takes place. Oxidation of Zr is logarithmic below 300 – 400 ^oC, which means weight increases with time and temperature. However, above 1000 ^oC, only parabolic behavior has been reported. Above 600^oC ,dissolution is governed by diffusion in Zr (52).

ZrO_2 exist in three modifications namely, monoclinic (below 1000 – 1200^oC), tetragonal at higher temperature and cubic above 1500^oC. At temperature below 600^oC, non-lattice diffusion may be responsible for cubic behavior. It has been reported that after initial protective oxidation, Zr begins to oxidize at an accelerated rate. Diffusion through the oxide is proposed to take place along the preferred paths. Zr reacts rapidly at 800^oC to form zirconium nitride. ZrO_2, ZrN and ZrO are stable up to1500C. Zr removes gases like O_2, N_2, CO, CO_2, and H_2O at 1000^oC. In case of Ti, TiO_2, TiN and TiC are stable up to transition point. Energy of activation for oxidation reaction has been found to be 18.2 K.Cal / mol for Zr in the temp range of 200 – 425 ^oC, which is lower for Zr oxidation than Ti. For Ti oxidation governing mechanism is diffusion of nitrogen into metals in presence of a thin but permeable nitride film. Higher oxidation rate of Zr in air can be explained, if it is assumed that nitrogen dissolves in ZrO_2. Since nitrogen is quadri -valent, it would create defects in oxygen ion structure, permitting higher rate of diffusion of oxygen through ZrO_2. A similar suggestion has been made by Wagner etal (53). According to these authors three oxides Zr_2O, ZrO and Zr_2O_3 along with ZrO_2 are formed on Zr surface. As compared to Ti, Zr dissolves larger amount of oxygen (54).

While studying metal combustion in explosives and propellants, Halma (55) observed that Al starts igniting at 2200 – 2300 K. Mg evaporates easily and melts at low temp. It was found that burn rate coefficient of Mg – Al was smaller than that of pure Mg or pure Al. It appears Mg – Al alloy based propellants are easily ignitable. Combustion rate coefficient of Zr is of the same order as these of Al and Mg powder based propellants and burn rate coefficient is dependent on specific surface area. Zr and Ti are expected to behave like Mg and Al, as both metals are non-volatile in temp. range involved in combustion and both do not firm protective oxide coating.

Gany etal (56) are of the opinion that condensed phase reactions and processes occurring at fuel grain surface have major effect on over all combustion characteristics of boron fueled SFRJ. Metal   loads of more than 30% may alter gas phase combustion reactions. Gas phase diffusion flame is likely to be less intense than pure hydrocarbon fuel, thus playing less significant role in overall combustion process and heat feedback mechanism .Glowing zones near propellant surface may be the site of special surface activity including sporadic ejection of hot metal particles in various directions.

If melting point of metal is in temperature range of burning surface of propellant, particle coalescence is possible. Concurrent fractures of oxides skins and flow of metal during coalescence results in an increased oxidation rate and ignition. Wherever melting point of oxide is greater than metal, metal oxide may dissolve in molten metal, as in the case of Zr. However, if oxide melting temp. is attained at propellant burning surface, oxide may cause particles to stick together as in case of boron. With high solubility of molten oxide in molten metal (Zr/ Ti), burning proceeds by diffusion of metal to the surface through oxide layer. However, due to low solubility of oxide and low interfacial surface tension between the oxide and metal (Al) oxide tends to accumulate on the surface and interact and exposes the metal. Both Zr and Ti oxides dissolve in metal, resulting in surface reaction and large oxide product particle (57). It appears that in case of Zr, luminous combustion leads to enhanced heat transfer by radiation and hence enhances burn rates. Some metallic elements yield much higher specific heat values as compared to hydrocarbons and hydrogen and specific thrust of different fuels is proportional to square root of specific heat values. Zirconium is a fuel, which demonstrates remarkably high specific thrust as Gany (28) has shown that specific thrust of a ramjet using Zr as a fuel at different flight numbers at sea level will be of the order of 2250 (Mach No 3) and 2500 (Mach No 4) at equivalence ratio of 1.4. These results are in agreement with our results (31). Reactions of Zr with air produce ZrO, ZrN in addition to ZrO_2. This provides additional energy to the system. Superfine Ti and Zr powder show remarkably higher ignitability and both have high volumetric heat of combustion, much higher than Mg. (58).

Thus, there is tremendous scope for R&D work on Zr and Ti and Ni based fuel rich propellants for ramjet applications. In addition to propulsion of projectiles, one can foresee an emerging trend for change in missile mission implying ramjet propulsion including SFRJ (Solid fuel ramjet propulsion). The demand for longer range flight without increase in the missile size results in the need for more energetic propulsion system. Ramjets are capable of producing much larger total impulse for the same amount of fuel and hence, SFRJ may be considered for missile applications like surface to air, air to surface and most importantly air to air and supersonic cruise missiles.

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2) PAPER -2 ATTACHED SEPERATELY, Title of the paper “STUDIES ON ZIRCONIUM BASED FUEL RICH PROPELLANTS”.